ORGANIC REAGENTS

JOHN F. FLAGG

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Organic reagents.

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Volume IV

Organic Reagents Used in Gravimetric and Volumetric Analysis

By JOHN F. FLAGG, PH. D.

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ORGANIC REAGENTS

USED IN GRAVIMETRIC AND VOLUMETRIC ANALYSIS

JOHN F. FLAGG, Ph.D.

Research Laboratory, General Electric Company
Schenectady, New York

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Organic reagents.

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PREFACE

The advances made in the study and use of organic reagents in the past three or four decades are well known to the analytical chemists. The entire field of inorganic analysis with the aid of organic compounds is indeed now vast, including as it does the many reagents used in qualitative and quantitative analysis, as well as numerous compounds used in more or less incidental fashion as adjuncts in inorganic analysis.

There can be no doubt but that the popularity of organic reagents is deserved. Their accomplishments are outstanding, their potentialities unlimited. The whole of present day analysis, qualitative and quantitative, is replete with methods using organic reagents for specific precipitations, sensitive detections, or the like.

Nor has descriptive literature in the field been lacking. Excellent and comprehensive treatises have been written, including those by Feigl (*Qualitative Analysis by Spot Tests; A Manual of Spot Tests; Specific and Special Reactions*), Mellan (*Organic Reagents in Inorganic Analysis*), Prodinger (*Organic Reagents Used in Inorganic Analysis*), and by Yoe and Sarver (*Organic Analytical Reagents*). Shorter monographs, such as those published by the G. Frederick Smith Chemical Company, or by Hopkin and Williams Ltd., of London, also contain much useful information pertaining to the field. Review articles describing the various aspects of the use of organic reagents are numerous, and the more comprehensive textbooks of analytical chemistry now devote considerable space to the discussion of organic reagents.

The writer has hesitated in making an excursion into a field so well documented. It has been pointed out, however, that a real need exists for a book dealing exclusively with the use of organic reagents in gravimetric and volumetric analysis. The use of organic reagents in colorimetric analysis, spot tests, etc., would not be treated, there being adequate coverage of these subjects in works by Sandell (*Colorimetric Determination of Traces of Metals*), Feigl (*vide supra*), and others. The function of this volume then is to describe the various organic reagents (precipitants) used in gravimetric and

volumetric analysis; to indicate the type of analysis in which they may be used; and to provide proved directions for their use.

As to the contents: The material is presented in two sections, one devoted to theory and one to applications. This is an obvious, though convenient, division—one which permits a certain amount of emphasis on fundamental similarities among the various reagents.

In the theoretical section an effort is made first to give a condensed picture of the organic chemistry involved in the use of organic reagents. Similar material is presented in much greater detail by Feigl, Yoe and Sarver, and others; only the fundamentals are considered here. Next, the physical and chemical properties of the compounds with which the analyst deals are considered. Particular attention is paid to those properties which are important in analytical work. A general review of the theoretical section reveals the dearth of really fundamental information regarding the chelate complexes and their use in analysis, and should suggest courses for further research. The section concludes with a chapter devoted to special techniques that are required in analysis with organic reagents.

The second section contains chapters devoted to a detailed discussion of various organic precipitants. All the well-known reagents that are used in gravimetric and volumetric analysis are included, as well as numerous reagents of as yet minor importance. Some reagents are discussed in great detail, as a voluminous literature pertaining to their use testifies to their importance. 8-Hydroxyquinoline is one of these. Others, such as thionalide, are relatively new but very promising, and the details of their use are given in the hope of stimulating research on further applications. It will be noted that most of the reagents are of the type that form chelate complexes. This class has been thoroughly studied, and seems to offer much in the way of general applicability. Such reagents are reasonably selective if not specific, and their compounds have desirable properties from the analytical standpoint. It is not intended to imply, by this selection, a secondary importance for the so-called penetration compounds. These have also received much study, but show few if any advantages over reagents of the former type. The use of organic solvents in gravimetric analysis was considered outside the scope of this book.

The chapters dealing with the individual reagents are designed to afford as complete a picture as possible of the behavior of the reagent: how it reacts with the various ions, what properties its complexes

have, and in what types of analysis it may be employed to best advantage. This has entailed a critical selection of methods which has, to a degree, been arbitrary. For a particular reagent, the methods for determining single elements in relatively simple mixtures are given. These are followed in many cases by methods for the analysis of some particular substance, such as an ore or alloy. These special methods have been included more to denote the scope of the reagent than to provide a compendium of analytical procedures, although naturally it is hoped that the methods given will prove to have practical value. The selection of these special methods was probably not unprejudiced. The book is written from the chemist's viewpoint, which frequently fails to consider the analytical problems of the biochemists, the metallurgists, and others. Nevertheless, the aim throughout is to present a sufficiently complete picture of the behavior of any reagent to enable the analyst in any field to adapt it to his problems.

Many of the methods given have been tested in the author's laboratory. Information regarding the accuracy and precision of methods is given wherever available. Other factors being equal, strong reliance has been placed on methods published by the National Bureau of Standards, and by the American Society for Testing Materials. Omitting the details of a particular method need not necessarily imply that the method is unreliable; it is hoped, however, that the methods given in detail include only reliable ones.

The book deals mainly with analysis on the macro scale; details of many micro methods have been omitted. For those interested, a reasonably complete bibliography of micro methods is included with each chapter.

The author has endeavored to make the bibliography complete and current, although he may have failed in some instances because of poor distribution of information during the past few years, or lack of close perusal of articles in fields not closely allied with chemistry. Survey of the literature has extended to early 1946. In the matter of the bibliography, the aid rendered by the Yoe and Sarver book, as well as the Hopkin and Williams Ltd. monograph, is freely acknowledged. The saving in time made possible by the use of their bibliographies was indeed great.

In glancing over the references included with each chapter, one cannot fail to be impressed by the large number of papers of Russian and German origin. The field of organic reagents, it would seem, has

elicited high interest from the analytical chemists of these countries. It is hoped that American interest and research will keep pace.

Of the numerous contributions to the preparation of this book the author wishes to acknowledge particularly those of Dr. I. M. Kolthoff and Dr. M. L. Huggins in making suggestions concerning some of the chapters; of various individuals and agencies for granting permission to quote from their publications; of his wife, Clarice B. Flagg, for help in preparing the indices; of Mrs. Dorothy C. McCarty for proofreading and checking of material; and of Mrs. June P. Kern for typing the manuscript.

John F. Flagg

Schenectady, N. Y.
February 1948

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GENERAL DISCUSSION

CHAPTER I

Organic Compounds as Precipitants for Inorganic Ions

Many varieties of organic compound have found application in analytical chemistry. These have been classified[1] broadly as solvents and wash liquids, substances used in neutralizations, organic oxidizing and reducing agents, indicators, primary standards, acidic and basic salt-forming compounds, photometric aids and substances used for the control of adsorption, diazotizing and coupling agents, and alkaloids and natural products. Of these compounds, however, those such as the indicators and primary standards are scarcely thought of as organic reagents in the sense that an organic reagent is a compound used for the detection or determination of organic or inorganic substances, and that a direct interaction between reagent and substance being determined usually occurs. The field is narrowed still more when we choose to consider only the acidic and basic salt-forming compounds and, indeed, this group will be considered only in part, for interest will center in those compounds forming salts that have been used successfully in gravimetric and volumetric inorganic analyses. This means that practically all compounds save those that form insoluble organometallic salts are excluded from consideration, and again interest must be confined to those of proven usefulness.

Included in the group of compounds to be considered are substances differing widely in constitution and mode of action, yet possessing the common property of forming insoluble organometallic salts under certain well-defined conditions. Some of these reagents form what might be considered "normal" (electrovalent) salts, and others, predominately covalent salts of the so-called inner-complex or chelate type. Still others combine with the inorganic substance in some obscure fashion, perhaps through a process involving adsorption. The chemical nature of the organic reagent is important in determining the type of

[1] According to the usage of J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*. Wiley, New York, 1941.

salt to be formed. In this chapter the unique features of some organic compounds that make them "organic reagents" in the sense used here will be pointed out, and from a study of these features, which usually take the form of certain reactive groups within the molecule, further advances in the architecture of organic reagents should come.

For combination between an inorganic substance and an organic reagent to occur, the need for an affinity might be thought of which, in the ideal case, is so highly selective that only a single substance (ion) reacts. This ideal is never attained, and the analyst compromises on selective, rather than specific, action.

Specific reagents (or reactions) are those which, under the experimental conditions used, are indicative of one substance (or ion) only. Selective reagents (or reactions) are those which, under the conditions used, are characteristic of a comparatively small number of substances (or ions).

One aim of research in this field is the discovery of compounds possessing a high degree of selectivity; another is the discovery of the causes underlying such selectivity.

While most organic precipitants are selective only, various means are known whereby the selectivity of a reagent may be improved. These include adjustment of the *p*H, and the use of agents which form complexes with the elements, which, otherwise, might interfere with the determination. The tartrates and cyanides are typical complex-forming agents; numerous examples of their use will be found throughout the second section of this book. The function of *p*H in making a reagent more selective is discussed in detail in Chapter III.

Within the organic molecule there is generally a single acidic or basic group, or a combination of these, that is the key to the reactions of the compound. Such groups include the hydroxyl group in its various combinations (as hydroxyl, carboxyl, arsonate, etc.), the amino group or other groups containing basic nitrogen, the carbonyl group, the sulfhydryl group, and many others. In cases in which the precipitation occurs through an adsorption process, the precipitant usually contains large numbers of hydroxyl or carboxyl groups. In these instances a less well-defined compound may be formed than when simpler organic molecules are used.

The following sections of this chapter are devoted to a discussion of the various types of organic precipitants, with special emphasis upon the groups within the molecule that are responsible for the selective action. The salt-forming reagents and their reactive groups will be

considered in some detail first, to be followed by a short description of the so-called adsorption precipitants and their mode of action.

I. Salt-Forming Reagents

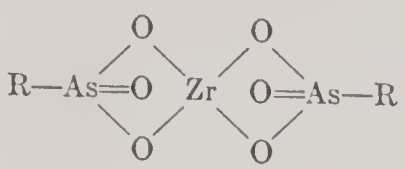
A. Precipitation of Normal Salts

A number of organic compounds form normal salts (with inorganic ions) of sufficient insolubility to make them valuable as organic precipitants. Such compounds may be of an entirely acidic or basic character, as contrasted with compounds to be considered later that show both acidic and basic functions. The acidic reagents, such as oxalic acid, the arsonic acids, picrolonic acid, and hexanitrodiphenylamine (dipicrylamine), may be selective under a given set of conditions only, or not at all. Thus, the arsonic acids are selective precipitants for zirconium in strongly acid solution, but at high *p*H they will precipitate many cations. Oxalic acid, on the other hand, exhibits scarcely any selective action, regardless of *p*H. The precipitants that are bases generally lack selectivity; among these are compounds like benzidine, nitron, and the tetraphenylarsonium compounds.

The following examples are chosen to indicate the type of salt formed in precipitations with this sort of reagent.

1. The Arsonic Acids, $R—As\begin{matrix}OH\\ =O\\ OH\end{matrix}$

These compounds combine with and precipitate the quadrivalent metallic elements in the fourth periodic group. The reaction occurs in rather strongly acidic solution. The arsonic acids themselves are weak dibasic acids, one or both hydrogen atoms of which would possibly be replaced in forming salts (I). Two moles of reagent combine with one mole of a metal such as zirconium; the salt may contain the tetra-



(I)

positive ion, or an oxygenated ion such as ZrO(II) (see also p. 108). The metallic arsonates are unsuitable for use as weighing forms, more perhaps because of difficulty in drying than because of uncertain composition.

The nature of the organic portion of the molecule influences the properties of the arsonic acids as precipitants. Thus phenylarsonic and *p*-hydroxyphenylarsonic acids precipitate both titanium and zirconium (among other elements) from strongly acidic solution, while *n*-propylarsonic acid precipitates zirconium, but not titanium under the same conditions. In acidic solution *p*-*n*-butylphenylarsonic acid precipitates ferric iron in addition to the quadrivalent elements.

The action of many other compounds containing the arsonic acid group has been studied; in general, their properties are similar. Substitution of the arsonic acid group by the arsinic acid group, —As$\langle^{OH}_{OH}$, does not alter qualitatively the behavior of the reagents. A list of compounds that have been prepared and studied is found in Table I.

TABLE I

Substituted Arsonic Acids

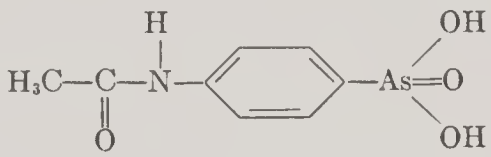
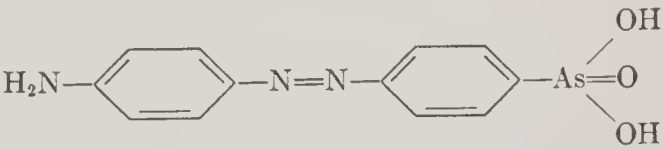
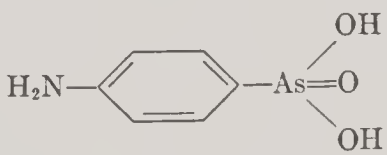
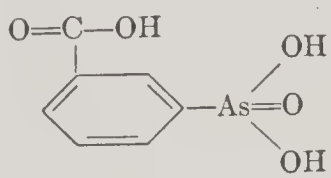
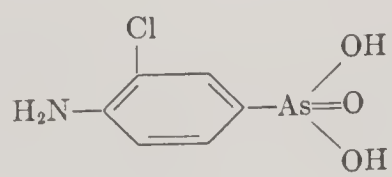
Name	Formula
Acetoarsanilic acid[a]	
p-Aminoazobenzenearsonic acid[b]	
Arsanilic acid[b-d]	
3-Carboxyphenylarsonic acid[d]	
3-Chloroarsanilic acid[d]	

TABLE I (*continued*)

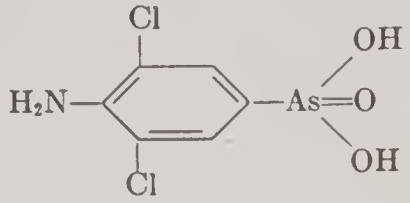
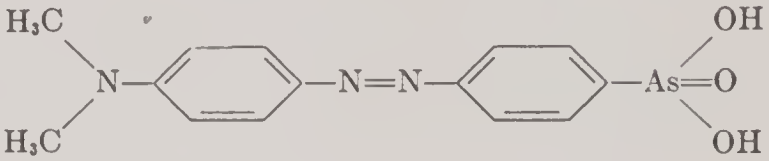
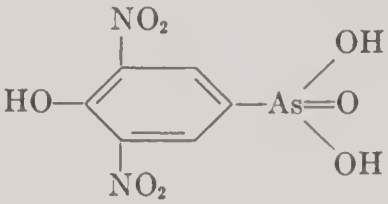
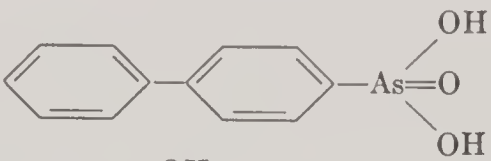
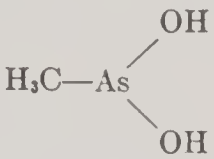
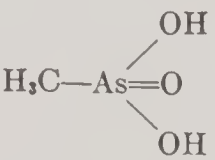
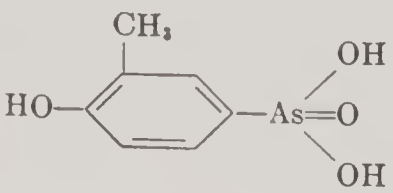
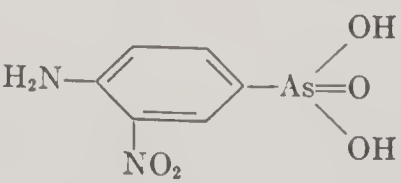
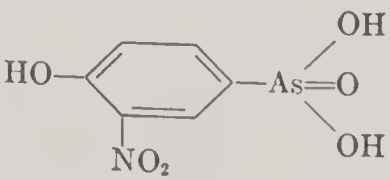
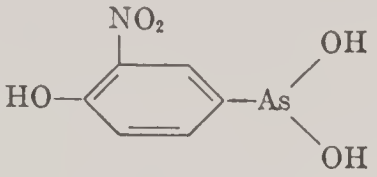
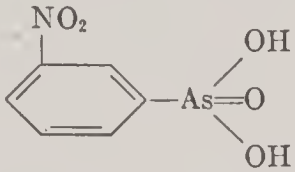
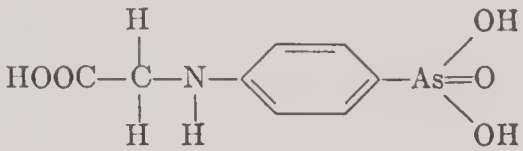
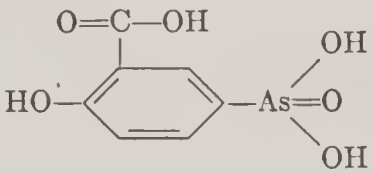
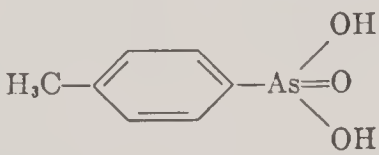
Name	Formula
Dichloroarsanilic acid[d]	
Dimethylaminoazobenzenearsonic acid[d, e]	
3, 5-Dinitro-4-hydroxyphenylarsonic acid[d]	
Diphenylarsonic acid[d]	
Methylarsinic acid[f]	
Methylarsonic acid[f]	
3-Methyl-4-hydroxyphenylarsonic acid[d]	
Nitroarsanilic acid[d]	
3-Nitro-4-hydroxyphenylarsonic acid[d]	

TABLE I (*concluded*)

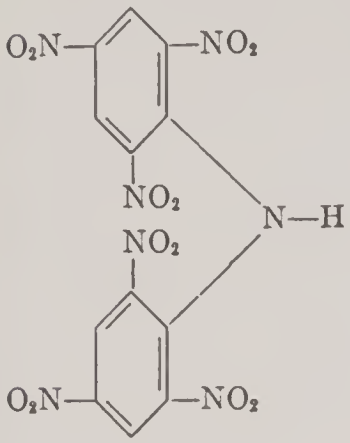
Name	Formula
3-Nitro-4-phenolarsinic acid[g]	
m-Nitrophenylarsonic acid[h, i]	
Phenylglycinearsonic acid[d]	
Salicylarsonic acid[d]	
p-Tolylarsonic acid[d]	

[a] H. J. Kapulitzas, *Dissertation*, Vienna, 1920.
[b] I. M. Korenman, *Z. anal. Chem.*, **90**, 115 (1932).
[c] J. F. Miller, *Ind. Eng. Chem., Anal. Ed.*, **9**, 181 (1937).
[d] F. Feigl, P. Krumholz, and E. Rajmann, *Mikrochemie*, **9**, 395 (1931).
[e] V. A. Nazarenko, *J. Applied Chem. U.S.S.R.*, **10**, 1696 (1931).
[f] R. Chandelle, *Bull. soc. chim. Belg.*, **46**, 283, 423 (1937).
[g] F. Pavelka and E. Kolmer, *Mikrochemie*, **8**, 277 (1930).
[h] F. Pavelka, *ibid.*, **8**, 345 (1930).
[i] B. Tougarinoff, *Bull. soc. chim. Belg.*, **45**, 542 (1936).

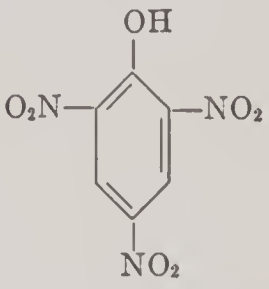
All compounds listed precipitate zirconium, and usually other elements as well. The most obvious differences are in color, although undoubtedly some differences in solubilities of the complexes would be observed. The 3-nitrophenolarsinic acid has been used to precipitate cadmium from acetic acid solution. Details of the applications of phenylarsonic acid, *p*-*n*-butylphenylarsonic acid, and *p*-hydroxyphenylarsonic acid are to be found in Chapter VII.

2. Acid Nitro Compounds

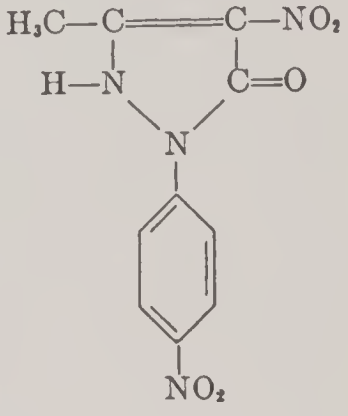
Included in this group are compounds such as hexanitrodiphenylamine (dipicrylamine) (II), picric acid (III), and picrolonic acid (IV). These substances react with a large number of metallic ions, particu-



(II)



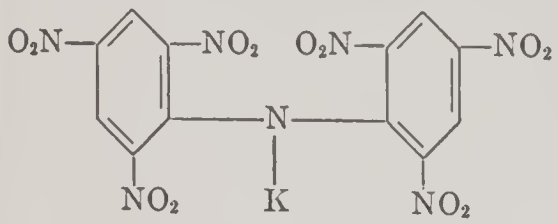
(III)



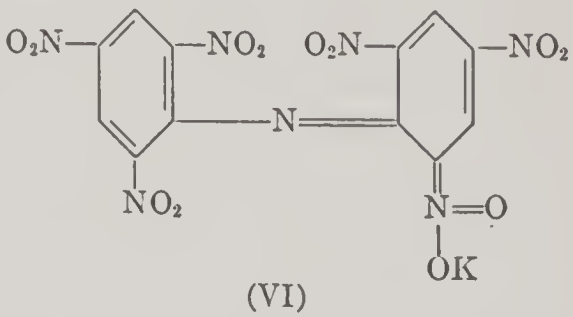
(IV)

larly among the heavy metals, although most of the studies on their use have been concerned with the precipitation of alkali metals or alkaline earths. The salts that are formed are probably electrovalent in all cases, especially since the alkali metals and alkaline earths do not ordinarily show chelation of the type encountered between reagents and cations to be considered later.

Dipicrylamine undoubtedly exists in resonance forms, and the salts could be considered as derivatives of either of these. Possible formulas for the insoluble potassium salt would be (V) and (VI):



(V)



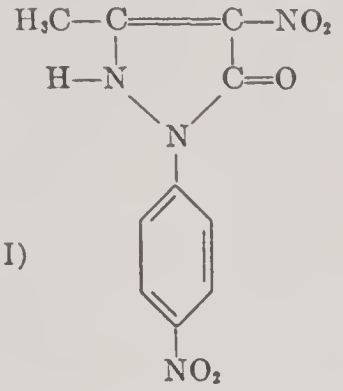
(VI)

The intense yellow-orange color of the potassium salt suggests that (VI) is the preponderant form.

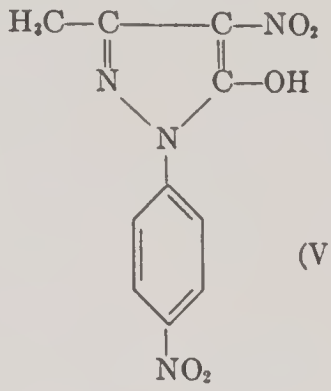
Picric acid, likewise a monobasic acid, forms insoluble potassium salts that have been used in analytical work. The picrates of many other metals are also insoluble and, like the potassium salt, are of pronounced color. Associated with the smaller molecular weight of picric acid, however, seems to be an increased solubility in water of

the picrates as compared with, say, the dipicrylamine salts; the latter are superior precipitation forms.

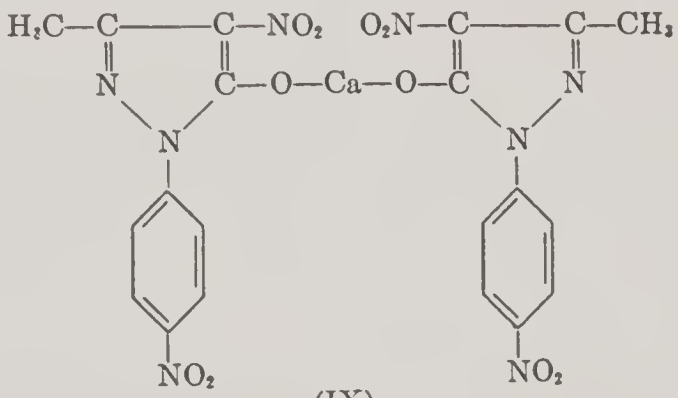
Picrolonic acid may exist in resonance forms (VII and VIII). It is monobasic, and the calcium salt, used for the gravimetric determination of that element (see page 219), may have formula (IX).



(VII)



(VIII)



(IX)

These reagents illustrate the fact that an increase in the acidity of an ionizable hydrogen atom, produced by the introduction of electronegative groups, enhances the reactivity of the compound toward metallic ions. In these cases the reagents have value, not because of a high degree of selectivity, but rather because they afford convenient weighing and precipitation forms for elements otherwise difficult to determine gravimetrically. Dipicrylamine possesses an added advantage of selectivity since it can be used for a separation of potassium and sodium. Picrolonic acid permits the separation of the alkaline earths from the alkali metals.

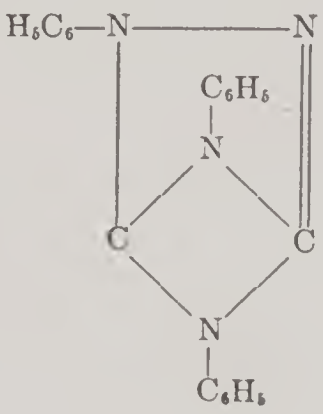
It is of interest to note that, generally, the reagents which precipitate potassium will also precipitate rubidium, cesium, and ammonium ions; furthermore, they usually do not precipitate sodium and lithium unless excessive amounts of these elements are present. This pronounced difference in solubility is noted not only in the organometallic salts, but also in the chloroplatinates, periodates, and perchlorates

when the potassium, rubidium, and cesium salts are of sufficient insolubility to permit their quantitative precipitation and separation from lithium and sodium.

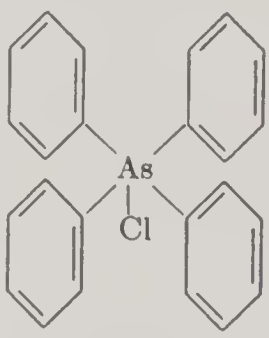
3. Anion Precipitants

The anion precipitants are basic compounds, usually of high molecular weight and containing nitrogen or arsenic. Three such reagents whose use will be discussed in later sections are benzidine (X), nitron (XI), and tetraphenylarsonium chloride (XII). The reaction of benzidine to form normal salts with sulfuric acid is the basis of a gravimetric method for sulfate. Other ions, such as phosphate and tung-

(X)

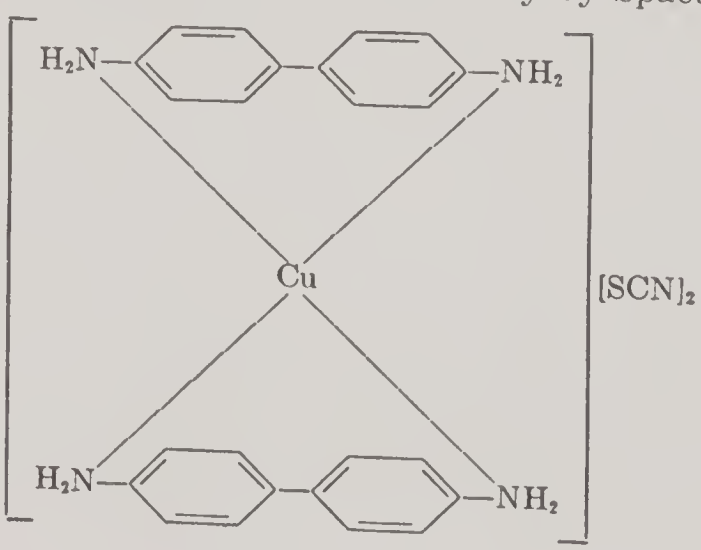


(XI)



(XII)

state, are precipitated by benzidine. Likewise, a number of metallic ions including cadmium, copper, mercury, silver, and zinc yield crystalline complexes with benzidine. In the latter cases the precipitates are of the general type (XIII). The use of such compounds in analytical chemistry has been studied intensively by Spacu and others.

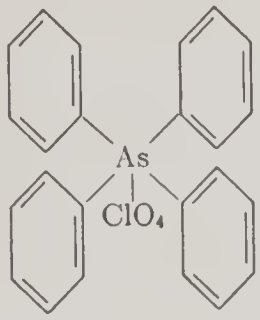


(XIII)

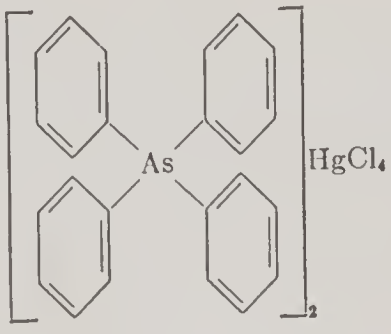
It has been found that pyridine, for example, forms insoluble complexes with cadmium, cobalt, copper, nickel, and zinc in the presence of thiocyanate ion, while the diamine complexes of copper may be used for the precipitation of cadmium or mercury as complex iodides. Comparatively few of these reactions, however, have come into widespread use. This probably reflects no lack of merit in the basic chemistry of the methods, but rather arises from the fact that they often require carefully controlled conditions for satisfactory results, and that the selectivity obtainable in so many organic reagents is lacking here. For a more extended treatment of these reagents and their use, reference should be made to Prodinger.[2]

Nitron forms an insoluble nitrate having the requisite properties of a gravimetric precipitate. Nitron is not a specific reagent, however, and many other ions including bromide, chlorate, chromate, nitrite, perchlorate, and perrhenate form insoluble salts.

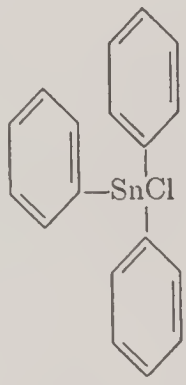
The arsonium compounds form normal salts with perchlorate, periodate, permanganate, and perrhenate ions, and may be used for their gravimetric determination. The reagents are not highly selective and other ions such as iodide, molybdate, and thiocyanate form insoluble salts; likewise, the chloro complexes of cadmium, tin(IV), and zinc. The formula of the perchlorate is illustrated in (XIV) and that of the chloromercuriate ion in (XV).



(XIV)



(XV)



(XVI)

Another type of anion precipitant is found in triphenyltin chloride (XVI), a reagent used for the gravimetric determination of fluoride ion. Triphenyltin fluoride is less soluble than the chloride, and precipitation of the fluoride occurs following a simple replacement reaction. The high molecular weight of the precipitate—and the corre-

[2] W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis.* Elsevier, New York, 1940.

spondingly favorable conversion factor for fluoride—is a decided advantage gained in using precipitants of this type.

B. Formation of Complex Salts

When an organic molecule containing both acidic and basic functions combines with a metallic ion, and if in the combination both functional groups are operative, a so-called inner-complex or chelate salt is formed. The general nature of the functional groups in organic reagents and the requirements for complex formation have been discussed in detail by Yoe and Sarver[1]; an extensive list of reactive groups has been given by Mellan,[3] and Diehl[4] has treated the subject of chelate rings in a general review article. The subject will be dealt with only briefly here, with the intention of indicating types of group that are important in the reactivity of organic precipitants, as well as general conditions under which the reactions occur.

1. Factors Influencing Complex Formation

Some important factors to consider in the formation of the inner-complex, or chelate, salts are: (*1*) the nature of the atoms or groups of atoms from which the ring will be built, (*2*) the size of the ring, and (*3*) the size of the ion entering the ring.

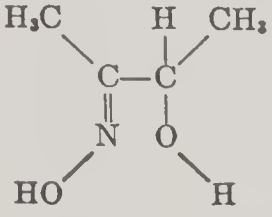
If an organic molecule is to form an inner-complex salt, it should contain an acidic group. The groups commonly regarded as acidic are hydroxyl, mercapto, and imino. (The carboxyl group is regarded as a special case of the hydroxyl group, attached to a carbonyl group.) From these more or less weakly ionized acids, hydrogen ion is replaced by metal. The ring is usually completed by the action of some other atom, such as nitrogen or oxygen, in the molecule forming a second covalent bond with the metal. The size of the ring is limited by considerations of geometry to from four to seven members, with five- and six-membered rings most favored. The requirements of the strain theory in this connection are well known, and it need only be stated that the heterocyclic rings containing metal conform in general to these requirements.

What influence the size of the cation has on the ease of complex formation has not been much investigated. Rough calculations, from data on bond angles and interatomic distances, indicate for example

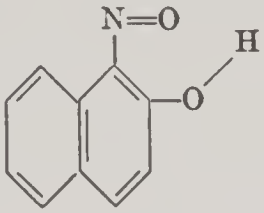
[3] I. Mellan, *Organic Reagents in Inorganic Analysis*. Blakiston, Philadelphia, 1940.

[4] H. Diehl, *Chem. Revs.*, **21**, 39 (1937).

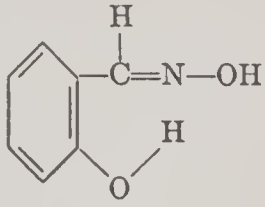
that in the compounds α-benzoin oxime (XVII), α-nitroso-β-naphthol (XVIII), and salicylaldoxime (XIX), a space of about 2.5 Å. is available in the reactive group for occupation by the metallic ion. The



(XVII)



(XVIII)

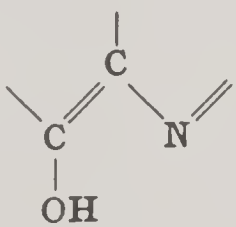


(XIX)

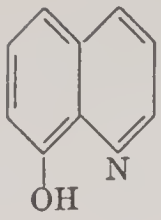
radii of the transition elements are of the order of 0.8 A. for the ions in crystals and most of the transition elements combine with these compounds, forming definite complex salts. These ions also possess vacant orbitals, necessary for the formation of homopolar bonds, and this factor is undoubtedly of importance in forming chelate complexes (see p. 44). The larger ions, such as bismuth and lead, often tend to form basic salts, or salts of indefinite composition during the course of the reaction. This might be interpreted in terms of incomplete chelation, caused by an ion too large to fit into the reactive group. The smaller cations are of course hydrated, so that their ionic radii in solution are probably larger than those observed in the crystal, but at least the dimensions are comparable with those of the groups to which the ions eventually become attached. It would thus seem that there may be some relation between ionic radius and space available within the group, and that this bears on the reactivity of organic compounds toward metallic ions. For the time, however, the approach to such problems remains largely qualitative.

2. Reactive Groups in Reagents

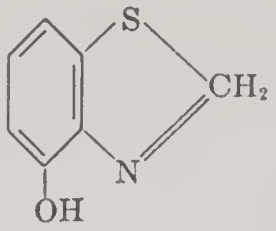
The following reactive groups are found among the reagents used in gravimetric and volumetric analysis:



This group appears in 8-hydroxyquinoline (XX) and its derivatives, and in 4-hydroxybenzothiazole (XXI). The functional groups

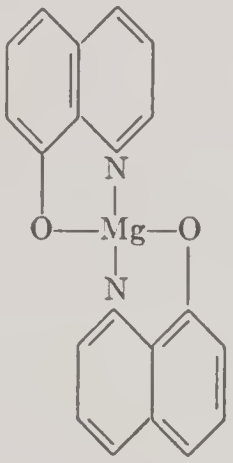


(XX)

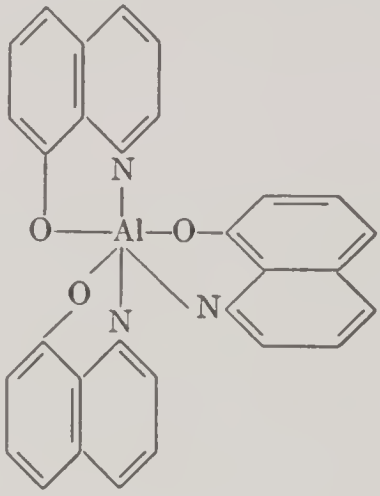


(XXI)

are hydroxyl and heterocyclic nitrogen; in 8-hydroxyquinoline the former is weakly acidic ($K_a = 10^{-11}$), the latter is weakly basic ($K_b = 10^{-10}$). Reaction with metallic ions results in the formation of two, three, or four five-membered rings, depending on the valence of the metal, with the metal common to each (XXII, XXIII). Many



(XXII)



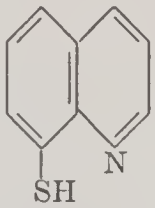
(XXIII)

di- and trivalent ions combine with this grouping, as do a few tetravalent ions such as thorium and zirconium. Selective precipitations are gained by control of the *p*H, or by the use of agents which form complexes. Various substituents, such as Br, I, CH_3, may be introduced in the ring system without altering qualitatively the function of the reactive grouping. Generally, the introduction of substituents other than acidic groups lowers the solubility of the complex and of the reagent itself in water. In many cases the colors of both reagent and precipitate are altered, as studies on various substituted 8-hydroxyquinolines have shown.[5,6]

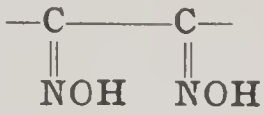
The mercapto derivative corresponding to 8-hydroxyquinoline

[5] G. Gutzeit and R. Monnier, *Helv. Chim. Acta*, **16**, 233, 2478 (1933).
[6] T. Boyd, E. F. Degering, and R. N. Shreve, *Ind. Eng. Chem., Anal. Ed.*, **10**, 606 (1938).

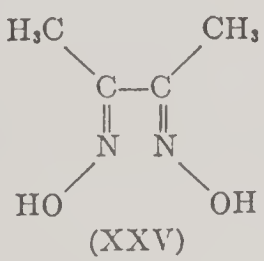
(XXIV) has been prepared and its reactions have been studied.[7] The acid group is apparently much weaker than in 8-hydroxyquinoline; insoluble complexes of cobalt, copper, nickel, palladium, platinum, and silver are formed in alkaline solution. However, the reagent is easily oxidized in air and is not suitable for general analytical use.



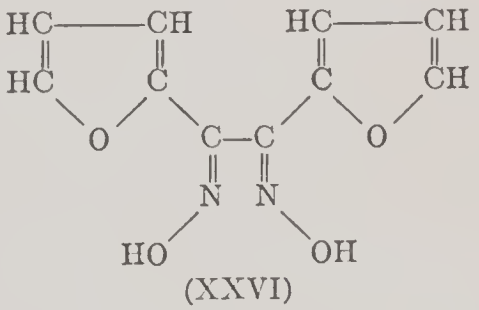
(XXIV)



The well-known dioxime group exhibits a fairly selective action for nickel, provided that the group is in an aliphatic system and has the α (anti) geometric configuration. Substituents which confer desirable properties of high molecular weight, solubility, etc., may be introduced into the molecule in which the group resides without alteration of the qualitative behavior of the reagent. Thus, replacement of the methyl groups in dimethylglyoxime (XXV) with furan groups to form furil dioxime (XXVI) increases the sensitivity of the reagent for nickel about threefold.



(XXV)



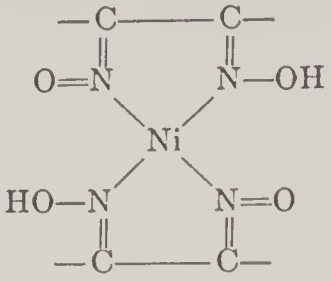
(XXVI)

The α-dioxime group also reacts with iron(II) and palladium(II) salts, and, when the group is part of an aromatic system, it acts as a dibasic acid to form salts with many metals.

In the reaction with nickel, two molecules of reagent combine with

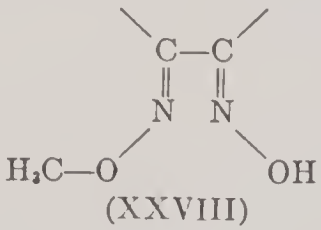
[7] J. R. Taylor, *Virginia J. Sci.*, **3**, 289 (1943).

a single ion of nickel; two five-membered rings are formed with the nickel atom in common (XXVII). It has been shown that only in the

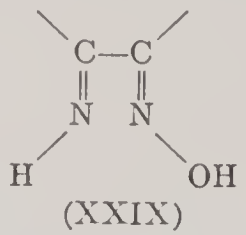


(XXVII)

case of the *trans*-dioximes (OH groups directed away from each other) are red precipitates formed with nickel ion. One hydrogen from each grouping is replaced, as shown by the fact that one of the oxime groups can be methylated (XXVIII) or replaced by an imino or methylimino group (XXIX), yet the molecule retains the property of forming a red

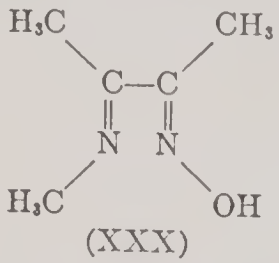


(XXVIII)

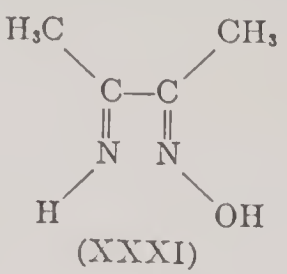


(XXIX)

precipitate with nickel. Thus, methyliminobiacetyl monoxime (XXX) and iminobiacetyl monoxime (XXXI) yield precipitates indistinguish-

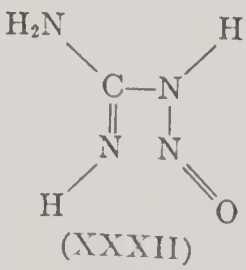


(XXX)



(XXXI)

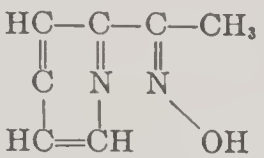
able from nickel biacetyl dioxime. Furthermore, a compound such as nitrosoguanidine (XXXII), in which one of the resonance forms is an



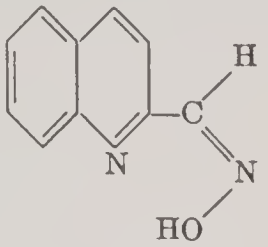
(XXXII)

oxime group, yields a red precipitate with nickel. Evidently the five-membered ring need not contain two carbon atoms.

In other cases a heterocyclic nitrogen atom can function in the chelate ring. Thus 2-pyridylmethyl ketoxime (XXXIII)[8] and quinoline 2-aldoxime (XXXIV)[9] yield red precipitates with nickel in ammoniacal solution.



(XXXIII)

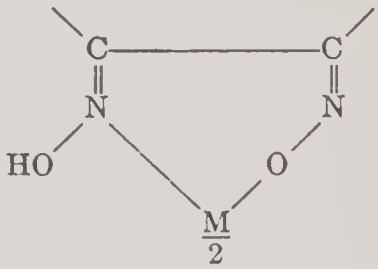


(XXXIV)

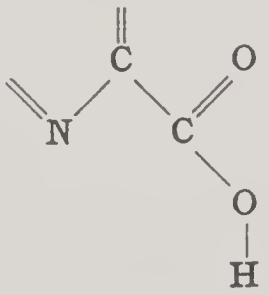
The β (or *syn*)-dioximes (XXXV) give no reactions with metals. The γ (or *amphi*)-dioximes (XXXVI) react with metallic ions but are much less selective than the α-dioximes. In complexes of the γ-dioximes the metal may be bound in a six-membered ring (XXXVII).

(XXXV)

(XXXVI)

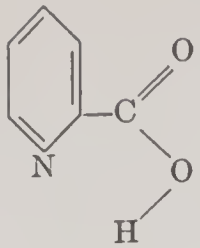


(XXXVII)

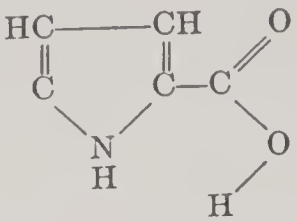


This grouping occurs in compounds such as α-picolinic acid (XXXVIII), 2-pyrrolecarboxylic acid (XXXIX), quinaldic acid (XL), and isoquinaldic acid (XLI). Compounds containing this group react with divalent metallic ions of the transition series, plus some other metals such as aluminum, lead, and mercury. The carboxyl group is moderately acid ($K_a = 10^{-5}$); there is probably relatively

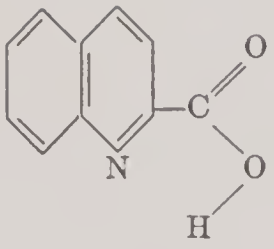
[8] B. Emmert, K. Diehl, and F. Gollwitzer, *Ber.*, **62**, 1735 (1929).
[9] T. W. J. Taylor, D. H. G. Winckles, and M. S. Marks, *J. Chem. Soc.*, **1931**, 2778.



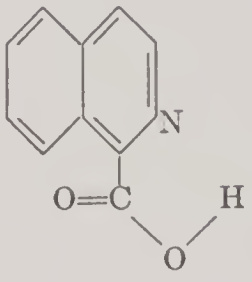
(XXXVIII)



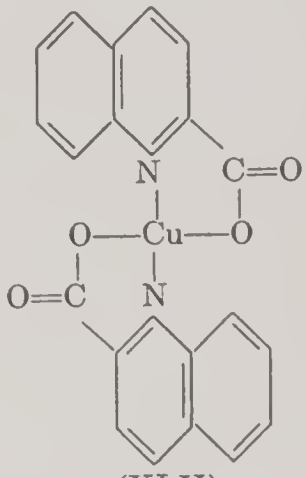
(XXXIX)



(XL)

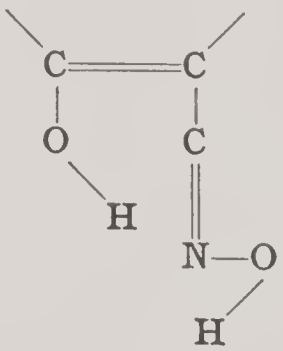


(XLI)



(XLII)

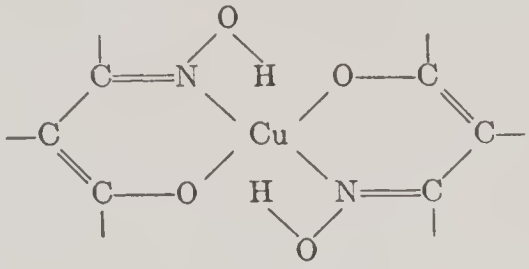
little dipolar ion formed in solution, at least in comparison with other nitrogen-containing groups such as occur in 8-hydroxyquinoline and anthranilic acid. In combining with a metal, the hydrogen atom is replaced, with the formation of five-membered rings. The light blue copper salt of quinaldic acid is (XLII).



This group shows a more or less selective affinity for copper in weakly acidic solution. Other metals, such as palladium, nickel, bismuth, zinc, gold, and lead ions, combine with organic compounds in which the grouping is part of an aromatic system, but many of these complexes are soluble in acid solution. Consequently, molecules con-

taining the group are satisfactory reagents for the separation and gravimetric determination of copper.

A number of compounds containing this reactive grouping have been prepared, and are listed in Table II. In chemical behavior toward inorganic ions they resemble one another, forming with copper a complex salt of the general type of formula (XLIII).



(XLIII)

TABLE II

Oximes of Similar Reactivity toward Metallic Ions

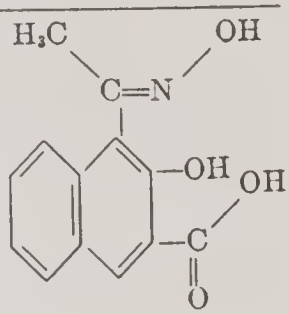
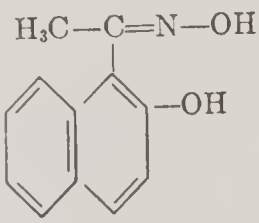
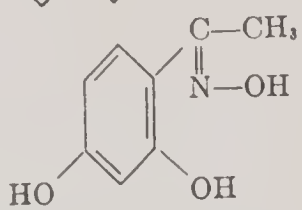
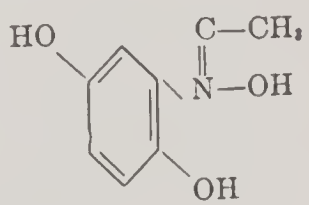
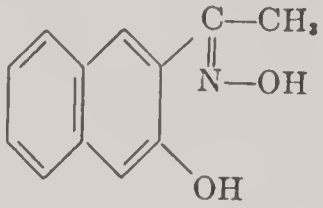
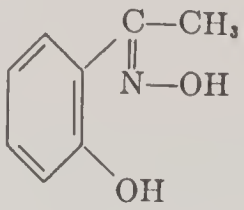
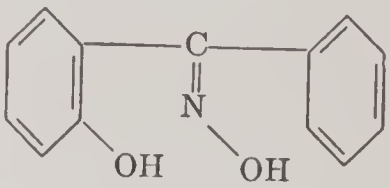
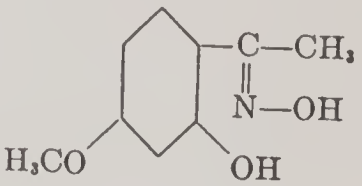
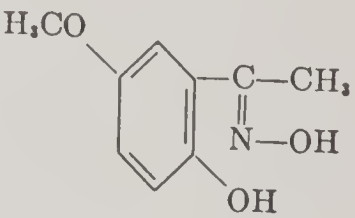
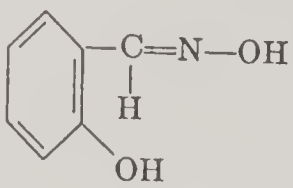
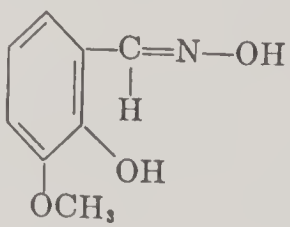
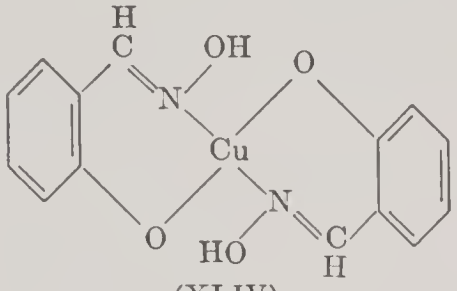
Name	Formula
α-1-Aceto-2-hydroxy-naphthoic acid (3)-oxime[a]	
α-1-Aceto-2-naphthol oxime[b]	
2-4-Dihydroxyacetophenone oxime[b]	
2,5-Dihydroxyacetophenone oxime[b]	

TABLE II (*continued*)

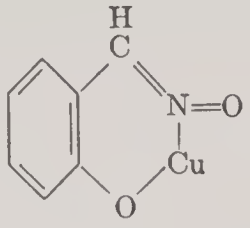
Name	Formula
2-Hydroxy-1-acetonaphthone oxime[b]	
2-Hydroxyacetophenone oxime[b]	
2-Hydroxybenzophenone oxime[a]	
2-Hydroxy-4-methoxyacetophenone oxime[b]	
2-Hydroxy-5-methoxyacetophenone oxime[b]	
Salicylaldoxime[b]	
o-Vanillin oxime[b]	

[a] F. Feigl and A. Bondi, *Ber.*, B54, 2819 (1931).
[b] F. Ephraim, *ibid.*, B54, 1210, 1215 (1931).

A divalent metal, such as copper, combines with two molecules of salicylaldoxime, a typical compound of this sort (XLIV). If the complex is treated with alkali, the reaction to yield product (XLV) takes



(XLIV)

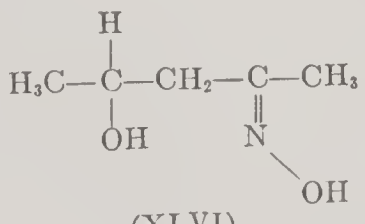


(XLV)

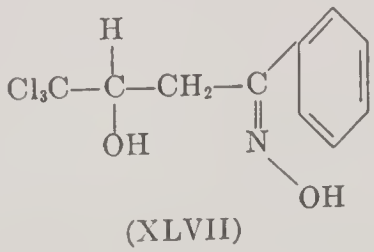
place. The same effect is obtained when the organic reagent is added to an alkaline solution of copper tartrate. In such a case the organic reagent behaves as a dibasic acid, presumably because the oxime tautomerizes to the nitrone form under the influence of alkali. The product containing one mole each of copper and organic reagent is converted back to the usual type of complex by the action of acetic acid. In the case of the zinc salicylaldoxime complex, the conversion from the di- to the mono-acid form is accomplished merely by heating in weakly alkaline solution.

That the bonding in compound (XLIV) is between metal and oxygen, and metal and nitrogen, has been demonstrated[10] by the fact that no complex is formed if the phenolic hydroxyl is blocked with a methyl group. If the methyl group is introduced into the hydroxyl of the oxime there is no effect on complex-forming ability. Thus it is concluded that salt formation involves bonding between metal and oxygen, and metal and nitrogen.

Oximes of aliphatic compounds such as acetonylcarbinol (XLVI) and chloralacetophenone (XLVII) form no complexes with copper even though the same number, kind, and arrangement of atoms is present in the reactive grouping. A more acidic hydrogen, such as that in phenols, is apparently necessary for the formation of complexes of this type.



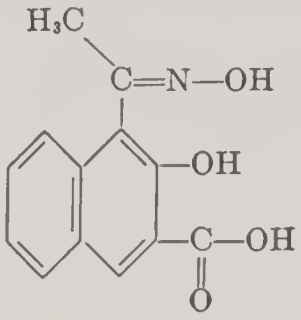
(XLVI)



(XLVII)

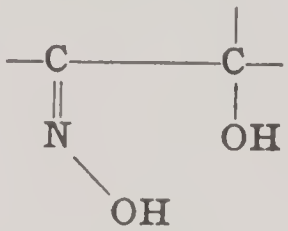
[10] F. Feigl and A. Bondi, *Ber.*, **B64**, 2819 (1931).

For immediate formation of complexes with metals the oxime must be of the α-configuration. In α-1-aceto-2-oxynaphthoic acid (3)-oxime (XLVIII), only the α-form reacts with copper acetate.[11] The β-form



(XLVIII)

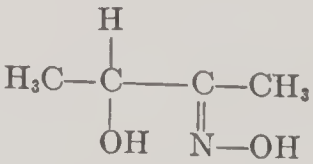
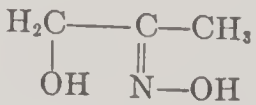
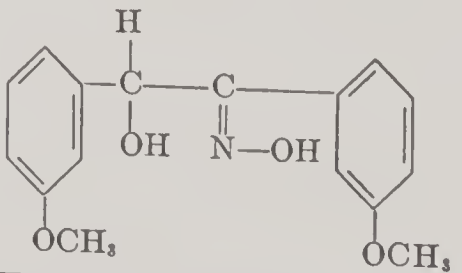
reacts only insofar as it is converted to the α-form. Salicylaldoxime exists only in the α-configuration, but for most of the others listed in Table II both forms are known.



This group, the acyloin oxime group, appears in a large number of compounds. Some of these are listed in Table III. A selective action

TABLE III

Oxines That Precipitate Copper from Ammoniacal Solution

Name	Formula
Acetoin oxime*	
Acetol oxime*	
Anisoin oxime	

[11] J. Meisenheimer, W. Theilacker, and O. Beisswenger, *Ann.*, **495**, 262 (1932).

TABLE III (*continued*)

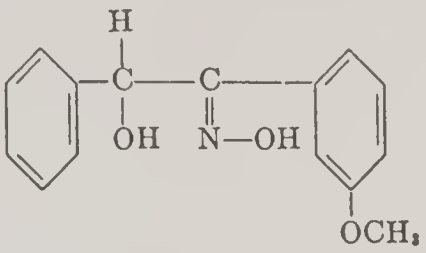
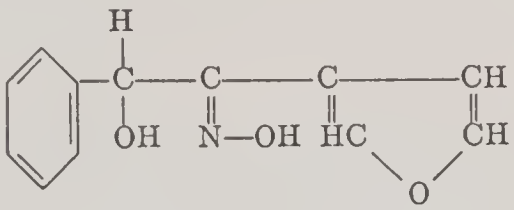
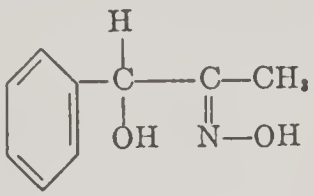
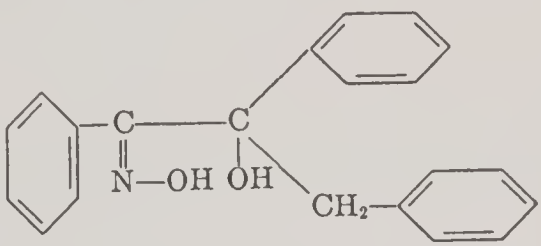
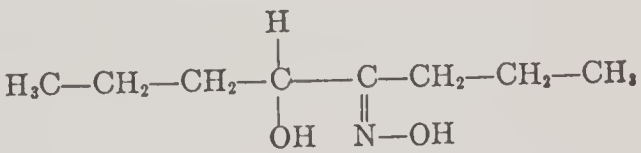
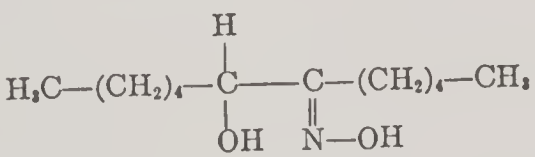
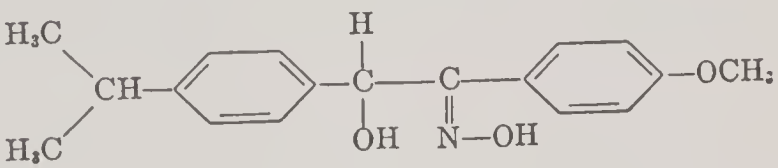
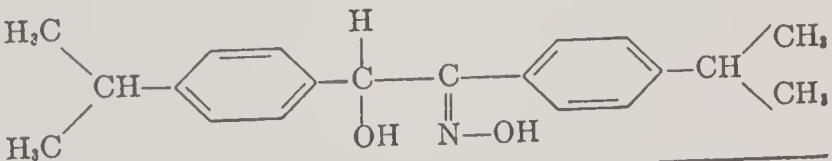
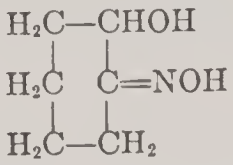
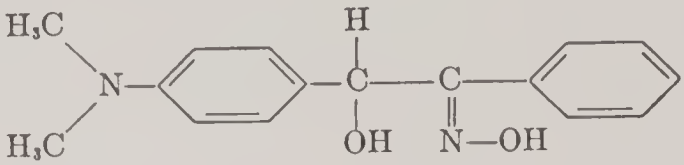
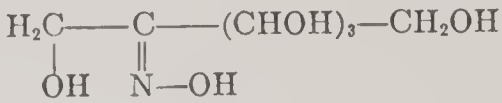
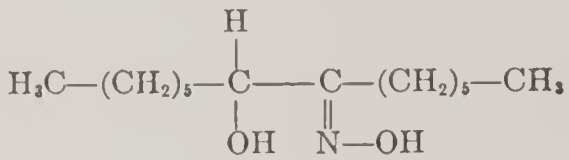
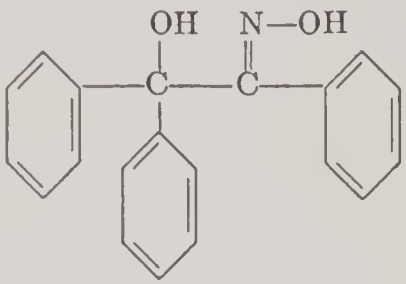
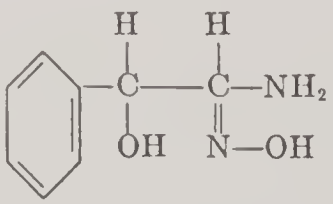
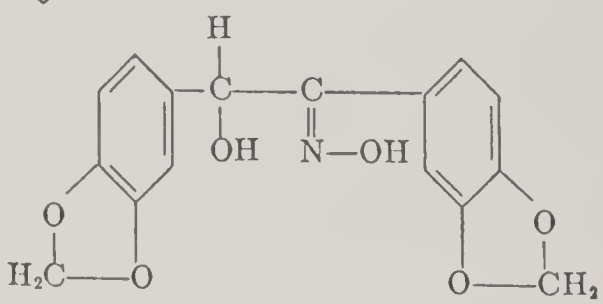
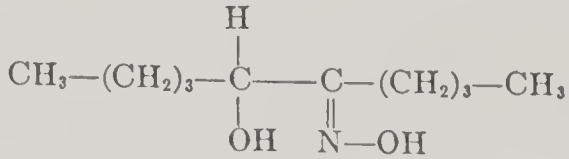
Name	Formula
Benzoanisoin oxime	
Benzofuroin oxime	
Benzoin oxime	
Benzylbenzoin oxime	
Butyroin oxime*	
Capronoin oxime	
Cuminanisoin oxime	
Cuminoin oxime	

TABLE III (*concluded*)

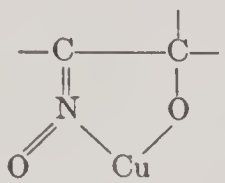
Name	Formula
Cyclohexanolone oxime	
p-Dimethylaminobenzoin oxime	
Fructose oxime*	
Oenanthoin oxime	
Phenylbenzoin oxime	
Phenylhydroxyethenylamide oxime	
Piperonyloin oxime	
Valeroin oxime	

* F. Feigl, G. Sicher, and O. Singer, *Ber.*, **B58**, 2294 (1925).

is shown by these compounds in that only copper is precipitated from an ammoniacal solution. The oxime must have the α-configuration for the selectivity to be maintained. The group functions as a dibasic acid, with the oxime group tautomerizing to the nitrone under the influence of alkali.

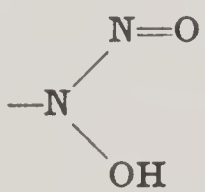
The tautomeric forms of the oxime are present in equal amounts at *p*H 6 in α-benzoin oxime; the acid dissociation constant[12] is about 10^{-6}. The formula of the copper complex of α-benzoin oxime is (XLIX). Certain of the complexes are insoluble in excess ammonia;

(XLIX)



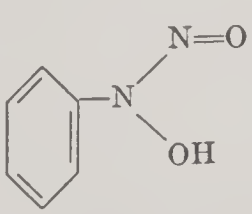
others (starred) dissolve, presumably with the formation of the tetrammine cupric ion.

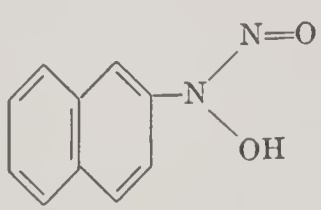
In acidic solutions, molybdate ion is precipitated by compounds containing the acyloin oxime group. The composition of the precipitates is unknown.



Phenylnitrosohydroxylamine (L) and naphthylnitrosohydroxylamine (LI) (cupferron and neocupferron) are reagents containing this grouping; they combine in a nonselective manner with many ions, including aluminum, bismuth, copper, iron, tin, titanium, uranium, vanadium, and zirconium. Reaction may occur in strongly or weakly acidic solution; the selectivity is somewhat greater under the former condition as only iron, tin, titanium, vanadium, zirconium, and tetravalent uranium precipitate.

(L)



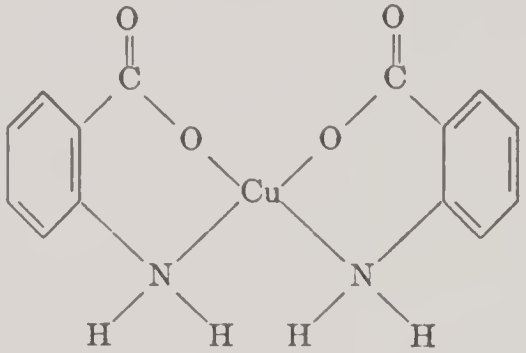


(LI)

[12] A. Langer, *Ind. Eng. Chem., Anal. Ed.*, **14**, 283 (1942).

The group contains an acid function, and may form five-membered rings in combination with a metal. The thermal instability of the complexes prevents their being dried and weighed for gravimetric analysis, and in general makes difficult their precise characterization.

The α- and β-amino acid groupings react with divalent elements of the transition series, and with others, to form analytically useful compounds. Anthranilic acid is a valuable reagent containing this reactive grouping; the formula of its insoluble copper salt is (LII). The copper



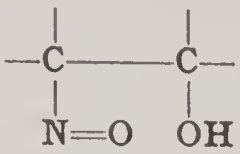
(LII)

salt of α-amino-*n*-caproic acid containing a similar ring system is also insoluble in water.

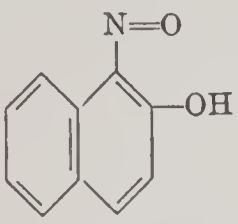
The carboxyl group in these compounds is moderately acidic, and, in view of the basic nature of the nitrogen atom, the formation of dipolar ions is possible. Chelation then, if it occurs, involves competition between the hydrogen ion and the metallic ion for the pair of electrons on the nitrogen atom. In a strongly acidic solution the tendency is away from chelation in that precipitates do not form, while the reverse is true as the *p*H is increased. A somewhat more quantitative picture is given in Chapter III in connection with separations.

The amino acid group in such compounds is naturally a center of interest because its behavior in combining with metallic ions in chelate rings has implications beyond those of analytical chemistry. The reactions of enzymes, for example, may well involve equilibria of this sort. Some studies along these lines have been carried out, and the equilibria in the zinc–glycine system have been described.[13]

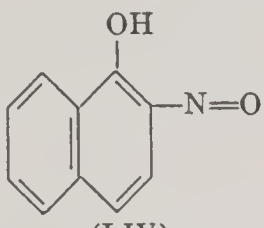
[13] I. Greenwald, *J. Phys. Chem.*, **47**, 607 (1943).



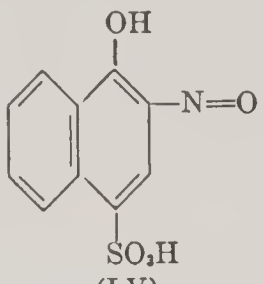
Among the reagents containing the nitrosonaphthol group are α-nitroso-β-naphthol (LIII), β-nitroso-α-naphthol (LIV), β-nitroso-α-naphtholsulfonic acid (LV), and nitroso R salt (LVI). The hydroxyl group is acidic and the reagent functions as an acid, combining with many di- and trivalent ions in an acetic acid–sodium acetate buffer. A tautomeric form (LVII) for the grouping is also possible, although



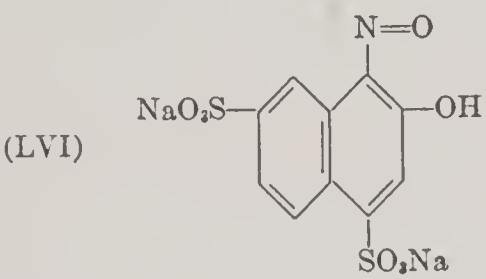
(LIII)



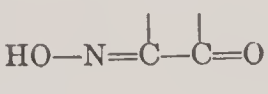
(LIV)



(LV)



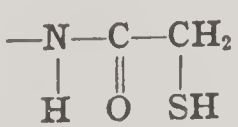
(LVI)



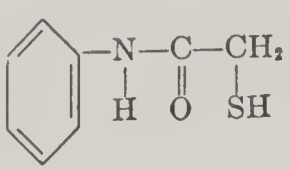
(LVII)

it is rather unlikely that the salts precipitated from acid solution are derivatives of that form.

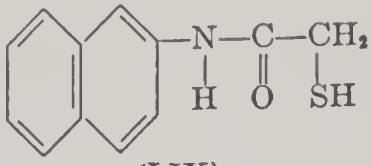
Much fundamental information regarding the composition of the cobalt and copper salts of α-nitroso-β-naphthol has been obtained from polarographic studies (for details, see page 208). It appears, however, that at least two molecules of precipitant combine with a single divalent cation. Precipitates formed by reagents of this general class are seldom weighed directly, and, since their composition and stability are uncertain they are ignited.



The thioglycolic acid grouping is found in thioglycolic acid anilide (LVIII), and in thionalide (LIX), both of which act as precipitants

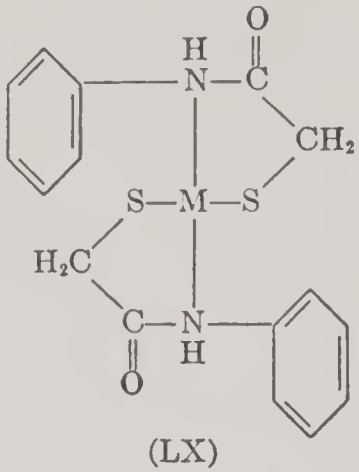


(LVIII)



(LIX)

for metals of the hydrogen sulfide group. The precipitations are non-selective, but the reagents have value in that the complexes are stable and of very low solubility. The sulfhydryl group functions as an acid; presumably five-membered rings are formed with the metal common to each (LX). The increased stability of the SH group toward oxidation is noticeable, particularly as compared to 8-mercapto quinoline.



(LX)

C. Summary

Certain common features can be observed in these organic reagents used for making gravimetric determinations. Insoluble salts of the alkali metal and alkaline earth elements are formed by those compounds in which a hydrogen atom, activated by nitro groups, is moderately acidic and may be replaced by the metallic ion. Precipitation of the heavier elements in these groups is favored.

Among the reagents that form chelate complexes, the presence of an atom of nitrogen in the molecule is almost always required. The molecule must also contain an acidic group which, with nitrogen and metal atom, forms rings usually having five or six members. A few geometrical requirements must also be satisfied. These requirements should be considered in a search for new reagents, but they should not become restrictive. Many reagents remain to be discovered, some undoubtedly superior to existing ones, and, at this early stage in our understanding of the nature of chemical affinity, it is well to be unhampered by what may yet prove to be an incomplete set of rules.

II. "Adsorption" Precipitants

A number of organic reagents used in quantitative analysis react with inorganic ions in a manner much less easily explained than those already discussed. Reagents such as tannin, cinchonine, and the anthraquinones are of this category, and, because one cannot write a simple chemical equation that describes their reactions, they are often called "adsorption" reagents or precipitants. The term adsorption is used not without some justification, although it is largely a disguise for ignorance of basic facts.

The anthraquinones and related compounds are much used in colorimetric analysis, particularly in the determination of trivalent elements, such as aluminum and chromium, with which highly colored lakes are formed. Tannin is used in gravimetric analysis as a precipitant for metals that form insoluble hydroxides or basic salts, while cinchonine and related alkaloids are used to reduce the solubility of tungstic oxide in the gravimetic determination of tungsten.

The "adsorption" reagent may function by direct chemical combination with the ion being determined; it may combine with some compound of the element sought by a physical process; or its action may involve both processes. In the first case it would be expected that normal or chelate salts would be formed, and that these would resemble other compounds of that class. In the second case the interaction would be primarily that of two colloids involving mutual flocculation.

There is evidence that, in the reaction of the anthraquinones with aluminum, the combination is nonstoichiometric. Probably in this case both chemical combination and adsorption occur.[14] The hafnium–alizarin lake, however, is shown to be a true compound containing hafnium and alizarin in a 1:1 mole ratio. Very little adsorption of excess dye on the lake is found in this instance.[15] Precipitation by tannin very likely is a colloidal process only. Tannin precipitates only the metals that form hydroxides, or basic salts of a low degree of solubility. These include aluminum, beryllium, chromium, iron, tin, titanium, uranium, vanadium, and zirconium. Precipitation does not occur when tannin is added to an acid solution of the ions of the metal, but only when the *p*H is made sufficiently high to precipitate a basic salt or hydroxide.

[14] E. E. Porter and H. B. Weiser, *J. Phys. Chem.*, **31**, 1383, 1704 (1927).
[15] H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.*, **69**, 1130 (1947).

Tannin itself is a negatively charged colloid, while the hydroxide sols are positively charged. The mechanism of the precipitation may thus involve a flocculation process, brought about by the adsorption of the tannin on the hydroxide sol. Presumably the glucose end of the tannin molecule would be more readily adsorbed than the digallic acid end. Thus the digallic acid portion of the molecule would be directed toward the water, but, as this portion of the molecule is only weakly hydrophilic, flocculation of the colloids could occur. The value of this type of precipitant lies in the fact that comparatively small amounts of material can be recovered quantitatively from large amounts of solution.

CHAPTER II

Some Properties of the Organometallic Precipitates

The compounds employed in quantitative analysis with organic reagents are members of the large class of organometallic compounds, the greater part of which are of no immediate importance in analytical work. Our interest in these compounds is confined to special cases in which unusual physical and chemical properties make them useful in qualitative and quantitative analysis. A complete description of the field of organometallic compounds, or even all the chelate complexes with which the analyst deals, is naturally beyond the scope of this book.[1] The purpose of this chapter is to describe the physical properties of a few complex compounds resembling those whose application will be treated in later sections of this book.

The physical properties to be dealt with include structure, solubility, stability, and color. Some of these properties are of theoretical interest only, and have little direct bearing on the performance of quantitative chemical analyses with the aid of organic reagents. Their inclusion seems justified on the grounds that a knowledge of these properties will contribute to the fundamental understanding of the compounds used, and may thus lead indirectly to the development of new types of reagents, or to better uses for those already available.

A. Color

The relationships between color and chemical constitution in organic compounds have been extensively studied; the current viewpoint in terms of resonance has been summarized by Lewis and Calvin.[2] The color of organometallic complexes is determined in part at least by the type of bond present in the molecule. In the case of the organometallic precipitates, the color may be determined by either the anionic or cationic constituent of the molecule, or both in an occa-

[1] For classification and general review, see H. Diehl, *Chem. Revs.*, **21**, 39 (1937).
[2] G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

sionally additive fashion. If the anionic constituent is colorless, or nearly so, the color of the complex will often be determined by that of the cation. Thus, anthranilic acid and quinaldic acid are both slightly colored in the pure states; however, they form blue copper complexes, pink cobaltous complexes, green nickel complexes, and nearly white zinc and cadmium complexes. The color of the simple (hydrated) cation does not necessarily appear in the insoluble complex, however, for both the iron(II) and nickel salts of colorless dimethylglyoxime are bright red. In this case, the particular chelate rings, containing the two nitrogen atoms attached to the metal, are necessary in the production of the color. Of interest is the fact that the palladium complex of dimethylglyoxime, which contains a ring system similar to that found in the nickel and iron(II) complexes, has the color of the palladium(II) ion, light yellow.

When the reagent (or its anion) is of pronounced color, the color of the complex may be modified accordingly; 8-hydroxyquinoline, which in solution is an orange-yellow color, forms yellow salts with aluminum, antimony, bismuth, cadmium, magnesium, and zinc—all colorless ions. The copper and nickel complexes are of a yellow-green hue; the iron(III) complex is a greenish black. Another highly colored reagent, dipicrylamine, forms a potassium salt of the same orange color as the reagent. An uncolored reagent, such as picrolonic acid, will usually form colorless salts with colorless cations such as calcium and magnesium.

The effect obtained in the production of colored complexes by alteration of the chromophoric groups in the organic molecule is well known, and is extensively used in qualitative analysis. The arsonic acids, as precipitants for zirconium, form colorless or only slightly colored precipitates. Introduction of the azo group (see page 108) into the arsonic acid molecule results in a great enhancement of the color, both of the precipitant and the complex. In this instance, the color of the complex is deeper than the color of the precipitant itself, with the result that qualitative analysis at low concentrations is easier. In this and similar cases, the reactivity of the organic molecule remains unchanged. Nitro groups also enhance color; the precipitates of nitrosalicylaldoxime and nitroquinaldic acid are usually deeper in color than those of the unsubstituted reagent.

In general, the color of a particular organometallic precipitate is of greater interest in spot test or colorimetric analysis than in gravimetric

and volumetric analysis. It may be necessary occasionally to consider color in performing volumetric analyses, in which the color change of an indicator must be observed. In such cases, of course, one would endeavor to avoid the use of a highly colored complex salt.

B. Solubility

The solubility of the organometallic complexes depends on the nature of the solvent, the general character of the molecule, and the temperature. The effect of *p*H on solubility, particularly in relation to separations, is discussed in Chapter III, page 50. The influence of hydrogen ion is most probably to affect the stability of the complexes (see page 53), and thus should be considered separately from the question of the inherent solubility of the complex.

The organometallic precipitates may be of two differing types: the normal salt, or the so-called inner-complex salt. There is ample evidence for considering the first type essentially electrovalent; the latter as covalent. These salts have in common a very low solubility in water and an appreciable solubility in numerous organic solvents, mostly the nonpolar ones. The inner-complex (chelate) salts dissolve in these solvents more readily than the normal salts—a fact often cited to show the covalent character of the chelates.

Examples of this type of solubility are numerous. Most of the hydroxyquinolates are readily soluble in chloroform and acetone; some, like the aluminum salt, are soluble in alcohol, though to a lesser degree. Chloroform is an excellent solvent for many other complexes, including those of α-benzoin oxime, dimethylglyoxime, quinaldic acid, anthranilic acid, and salicylaldoxime. The metallic cupferrides are soluble in ether; potassium dipicrylamine, in acetone. Solution in these cases is not accompanied by decomposition which occurs when the complexes dissolve in acids although some dissociation must occur. This is shown by the fact that, using radioactive indicators, exchange between the covalently bound metal atom and the free ions has been demonstrated in the case of some copper[3] and magnesium[4] complexes.

The solutions of such complexes often retain the color of the solute. The color, as well as the solubility, may be determined to a certain extent by the *p*H (see page 50). The readily soluble complexes are often extracted from an aqueous phase prior to their colorimetric determina-

[3] R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).
[4] S. Ruben, M. D. Kamen, M. B. Allen, and P. Nahinsky, *ibid.*, **64**, 2297 (1942).

tion or analysis by other means; extraction of the dithizonates for example is of importance in colorimetric analysis. The organometallic compounds may be obtained in macrocrystalline form upon slow evaporation of the solvent (chloroform is best) from such solutions.

Quantitative data on the solubility of the chelate complexes in organic solvents are for the most part lacking. Much might be gained by way of making separations if more such information were available.

Substituents in the organic portion of the molecule are undoubtedly a factor in determining solubility. The presence of easily hydrated groups, *e.g.*, the hydroxyl, carboxyl, or sulfonic acid groups, tends to promote water solubility, both of the reagent and the complex. An increase in the molecular weight, especially if due to the introduction of aliphatic or aromatic residues, will generally result in a decrease in the water solubility of both the reagent and the complex.

The influence of increasing molecular weight on solubility has been shown in a study of the sulfonates of calcium, barium, and zinc. This effect is clearly demonstrated by the data given in Table IV. Like-

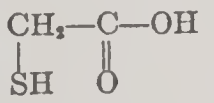
TABLE IV

Effect of Substitution in Decreasing Solubility[a]

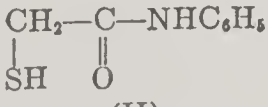
Element	Normality of a saturated solution of			
	Benzene sulfonate	Naphthalene 2-sulfonate	Anthracene 1-sulfonate	Anthracene 2-sulfonate
Calcium	1.74	0.0437	0.00048	0.00028
Barium	0.319	0.0069	0.00105	0.00007
Zinc	0.375	0.0096	0.00086	0.00013

[a] From data given by F. Ephraim, *Helv. Chim. Acta*, 8, 229 (1925).

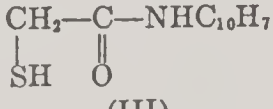
wise, Berg and Roebling[5] found that the solubility of the salts (copper, silver, and gold) of compounds (I), (II), and (III) decreased in that



(I)



(II)



(III)

order, *i.e.*, with increasing molecular weight. Other cases have been cited[6] which show similar effects.

[5] R. Berg and W. Roebling, *Ber.*, 68, 403 (1935).

[6] F. Feigl, *Specific and Special Reactions*. Elsevier, New York, 1940, pp. 144–151.

Since the solubility of most of the chelate complexes used in analysis is extremely low (at least in water), it need not be considered a major source of error in gravimetric work. The solubility may, of course, be reduced further by the use of an excess of precipitant. Some quantitative data on the effect of excess dimethylglyoxime on the solubility of nickel dimethylglyoxime are given on page 144. Another means for the reduction of solubility losses is the washing of the precipitate with a saturated solution of the same material; this is commonly done with the triple uranyl acetate precipitates of sodium.

The effect of temperature on the solubility of the chelate complexes in water would appear to be of negligible importance to the analyst, although again no quantitative data are available. The solubility of some of the normal salts, *e.g.*, potassium dipicrylaminate and nitron nitrate, is sufficiently great at room temperature to justify working with them at or near zero degrees.

C. Stability

The analyst is particularly interested in the thermal stability of the compounds with which he is working, particularly if gravimetric analysis is involved. This is especially important in the realm of organometallic precipitates, which contain an organic residue that is likely to be much more sensitive to heat than the conventional inorganic precipitate. Unfortunately, there have been no systematic studies on the thermal stability of the organometallic compounds used in analysis, or on any of these compounds. A few isolated cases are assembled here to indicate the nature and importance of the problem.

The effect of heat on an organometallic precipitate may be: (*1*) the removal of superficial water, (*2*) the removal of water of hydration, (*3*) the vaporization of the complex, or (*4*) the decomposition of the complex.

The first effect is of course desirable. For that purpose, temperatures of 100° to 110°C. are used; seldom does the complex decompose under these conditions. Occasionally, a lower temperature is used to dry precipitates that have been alcohol washed. The fact that a few complexes, such as the cupferrides, cannot be dried to constant weight, corresponding to a definite compound, under these conditions may indicate a low degree of thermal stability for that type of complex. The cupferron molecule itself is not particularly stable, and it might be expected that the instability would also be characteristic of the salts. The decomposition products in this case have not been

identified, but may include nitrobenzene, and some nitrogen oxides. In general, however, an organic compound is of limited use as a precipitant if its salts are thermally unstable. Hydrazoic acid and acetylene are cited as extreme examples.

Greater thermal stability is encountered in chelate complexes, the rings of which contain combinations of carbon, nitrogen, oxygen, sulfur, and metal. These include the oxyquinolates, anthranilates, and most of the complexes discussed in this book. Their salts are all stable at 100–110°; some are known to be stable at temperatures up to 160°C. The effect, if any, of an increase in temperature in this range is the removal of water of hydration. Aqueous tension data for the various hydrates of the complexes used in analysis are not known. A few cases, assembled in Table V, indicate the general types of hydrate obtained, and their thermal stability.

TABLE V

Degrees of Hydration of Some Organometallic Precipitates

Complex	Molecules of water of hydration at				
	25°	100°	125°	140°	160°
$Bi(C_9H_6ON)_3$	1	1	?	0	
$Cd(C_9H_6ON)_2$	2	1.5	0		
$Co(C_9H_6ON)_2$	2	?	0		
$Mg(C_9H_6ON)_2$	4	2	?	0	0
$Zn(C_9H_6ON)_2$	?	?	2	2	2
$Cu(C_{10}H_6O_2N)_2$	2	2	1		
$Zn(C_{10}H_6O_2N)_2$	?	1	1		

As higher temperatures are reached, volatilization of the complex or fission of the covalent bonds may occur. Nickel dimethylglyoxime sublimes without decomposition at 350°. Direct ignition of this and other organometallic precipitates should be avoided, as volatilization losses may occur. (Ignition under oxalic acid is recommended.) This relative ease of volatilitization is not unexpected in view of the covalent nature of the compounds. Frequently the complexes fail to melt, and, if they do not sublime, decompose directly into other products including the free metal or its oxide. Slow decomposition may begin at 200°C.

Information regarding the course of the thermal decomposition of such complexes is lacking for the most part. A study by Miller and

McLennan[7] on the behavior of magnesium hydroxyquinolate is one of the few on record. They found that during the dehydration at 160° of magnesium hydroxyquinolate dihydrate, a decomposition occurred resulting in a progressive loss in weight of the precipitate. The dried material was slightly hygroscopic, and, when treated with alcohol, could be freed of a yellow substance believed to be 8,8′-diquinolyl ether. They write the reaction for the decomposition as follows:

$$(C_9H_6ON)_2Mg \cdot 2\ H_2O \rightarrow MgO + (C_9H_6N)_2O + H_2O$$

In all cases of this type the reaction is undoubtedly complex. Lower oxides, or even free metal, are early end products of such decompositions.

A new approach to the subject of the stability of the chelate compounds has been taken by Calvin and Wilson.[8] They have studied the stability of various copper complexes of β-diketones and *o*-hydroxy aldehydes with respect to the reaction:

$$Cu^{++} + 2\ Ke^- \rightleftharpoons Cu\ Ke_2$$

in which Ke^- designates the organic anion. The object has been to ascertain the influence of the structural factors of the organic residues on the tendency to form chelates. In this particular case the compounds all contain a copper atom bound to four oxygen atoms.

A quantitative measure of chelation tendency is found in the constants K_1 and K_2, formation constants for the successive stages of the chelation process based on the assumption of a stepwise process in which Cu^{++}, $CuKe^+$, and $CuKe_2$ are present:

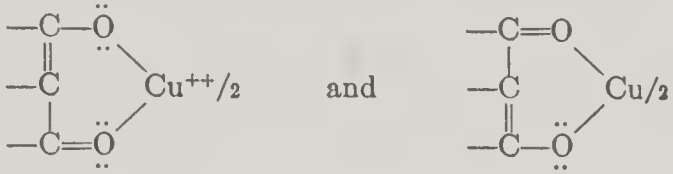
$$K_1 = \frac{[CuKe^+]}{[Cu^{++}][Ke^-]} \qquad K_2 = \frac{[CuKe_2]}{[CuKe^+][Ke^-]}$$

The constants are evaluated from experiments in which the *p*H is measured after titrating known amounts of Cu^{++}, chelating agent, and acid with a standard base. Interpretation of the results is based on the relative values of the constants, noting the effects produced by structural changes in the organic residues. The authors point out that differences in the constants might be expected, in general, to arise from differences in heats of reaction; since the ionic type of reaction remains the same throughout the series and the size of the organic anion does not vary greatly, hence the entropy of the reactions should be fairly constant.

[7] C. C. Miller and I. C. McLennan, *J. Chem. Soc.*, **1940**, 656.

On the basis of the results obtained, it is concluded that the binding forces in chelate compounds contain at least two components: (*1*) an ionic or coulombic component, containing the effect of charge and charge distribution of the anion as well as the charge and radius of the cation, and (*2*) a component involving the enolate resonance. The nature of the second component can only be speculated upon, although two interpretations have been suggested.[8]

(*1*) Copper ion, like the ions of the other transition elements, can accept an electron pair to form a homopolar bond. If an electron pair from each oxygen is allowed to form a homopolar bond with copper:



a rearrangement of the charges on the oxygen atom as shown would markedly enhance the energy contribution of the enolate resonance.

(*2*) A six-membered conjugated ring might be written that would be an important contributor:

In this case some question arises as to the availability and geometry of orbitals of the metal, and at present it is not possible to make a choice between the two pictures.

The importance of such studies for the future development of organic analytical reagents can scarcely be overestimated. It now appears entirely possible that, by choosing an organic compound whose enolate resonance is of the right order of magnitude, an organic reagent would be available for the purpose of combining selectively with a desired metallic ion. Thus the promise offered by organic reagents—a specific reagent for each element—may indeed have progressed a long way toward fulfillment.

D. Structure

The subject of structure of the chelate compounds has little practical importance for the analytical chemist. However, since considerable information is available regarding the structure of many of the

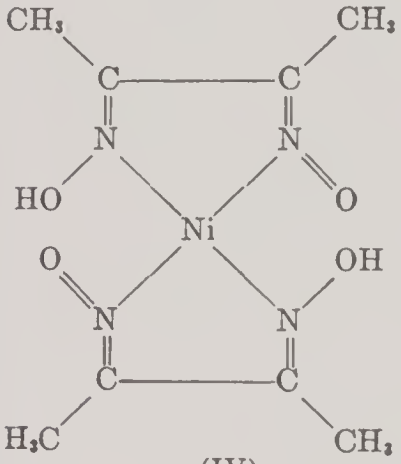
[8] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 67, 2003 (1945).

compounds to be discussed and used later, this information is included here as being of somewhat general interest. Also, it is not unlikely that such information will be important ultimately in fundamental studies on organic precipitants, and on chelate complexes in general.

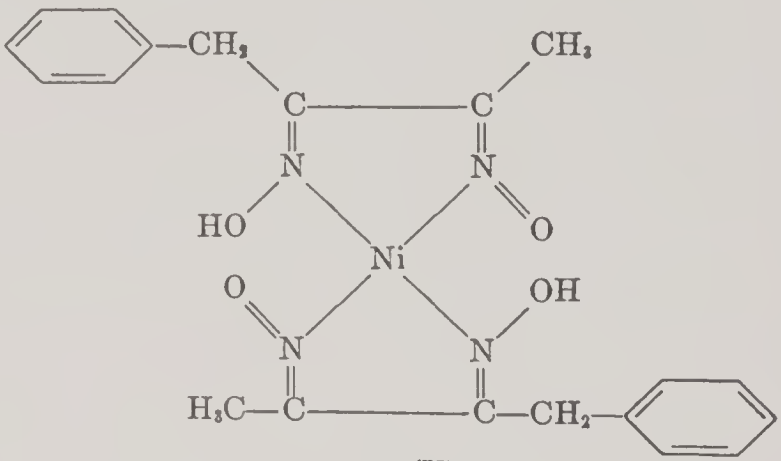
Knowledge of the structure of the organometallic complexes has come from three sources: (*1*) chemical studies, (*2*) x-ray diffraction (crystallographic) studies, and (*3*) magnetochemical investigations.

1. Chemical Evidence for Structure

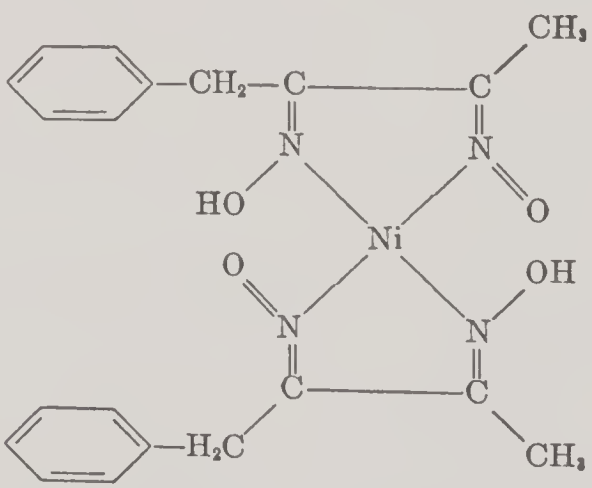
The existence of *cis-trans* isomerism has been shown in certain chelate complexes, among them the nickel glyoximes. Nickel dimethylglyoxime (IV) can exist in only one form. This is not the case with the unsymmetrical nickel glyoximes, such as benzylmethylglyoxime, which may have *cis* (VI) and *trans* (V) isomers. Sugden[9]



(IV)



(V)



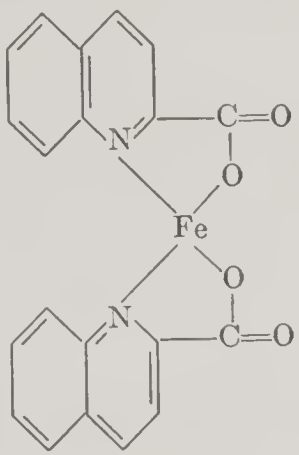
(VI)

was able to show that two such isomers existed; they were identical in molecular weight, but differed in melting point and solubility. The

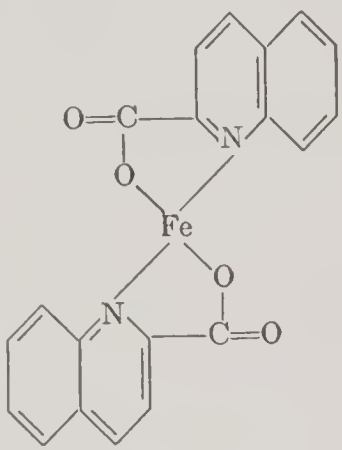
[9] S. Sugden, *J. Chem. Soc.*, 1932, 246.

alpha form melted at 168°, and was less soluble in acetone than the beta form, which melted at 75–77°. At 120° the beta form was converted into a mixture which contained both forms in equilibrium and which had a melting point of 152°. The isomerism was shown not to be due to stereoisomeric forms of the oxime itself; it was concluded that the two forms were geometrical isomers, and that the configuration was planar and not tetrahedral around the nickel atom. The lower melting isomer was thought to be the *cis* form. Tschugaeff also reported,[10] much earlier, the existence of isomers of this type.

An interesting case of what seems to be *cis-trans* isomerism is that of ferrous quinaldate. This compound exists in two forms: a red, unstable form which soon passes into a violet, stable form. The investigators[11] consider the red form (VII) to be *cis*, the violet form (VIII)



(VII)



(VIII)

to be *trans*. The existence of a planar molecule must be postulated to explain these observations.

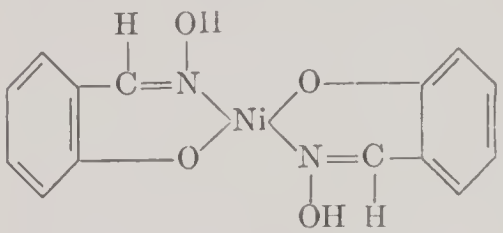
The existence of such phenomena should be considered in colorimetric work with organic reagents, particularly as the *cis-trans* isomerization may involve a pronounced color change, and may be a comparatively slow reaction. Many other interesting cases could doubtless be discovered.

2. Crystallographic Evidence of Structure

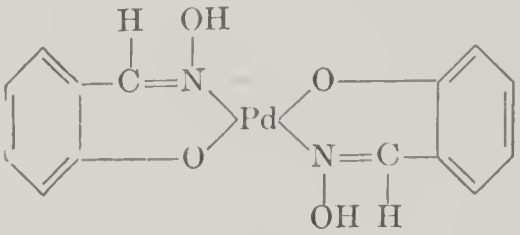
Extensive studies by x-ray diffraction indicate that many complexes of the type employed in analysis are planar—a confirmation of the

[10] L. Tschugaeff, *Z. anorg. Chem.*, **44**, 146 (1905); **46**, 144 (1905).
[11] P. R. Ray and M. K. Bose, *Z. anal. Chem.*, **95**, 400 (1933).

chemical evidence. The planar configuration for the quadricovalent complexes of nickel, palladium, and platinum with salicylaldoxime has been demonstrated.[12] The nickel and palladium complexes are isomorphous, have two molecules each in the unit cell, and are ascribed the *trans* configuration (IX, X).



(IX)

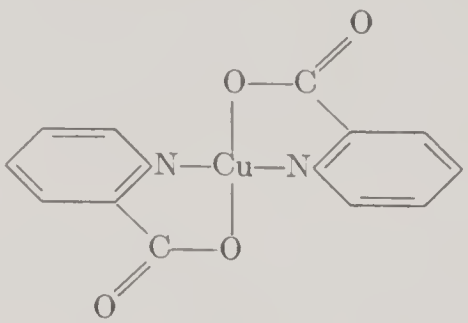


(X)

Further evidence for the planar configuration of the nickel complex lies in its diamagnetism (see page 44). Two types of platinum complex were found: $Pt(C_7H_6O_2N)_2$, which resembles the nickel and palladium salts and $Pt(C_7H_6O_2N)_2Cl_2$, in which the unit cell contains 32 molecules.

The nickel glyoximes are also planar. Both the dimethylglyoxime and the methylethylglyoxime complexes crystallize in the rhombic system, with two molecules comprising the unit cell.[13, 14]

The copper salt of α-picolinic acid (XI) has a planar configuration.[15]



(XI)

3. Magnetochemical Evidence for Structure

The covalent bonds formed in the organometallic complexes are the result of paired electrons. These electrons contribute nothing toward the permanent magnetic moment of the molecule.

[12] E. G. Cox, F. W. Pinkard, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, **1935**, 459.

[13] M. Milone, *Atti. congr. intern. chim., 10th congr., Rome*, **2**, 346 (1938); *Chem. Abstracts*, **33**, 7640 (1939).

[14] M. Milone and G. Tappi, *Atti accad. sci. Torino, Classe sci. fis., mat. nat.*, **75**, 445 (1940); *Chem. Abstracts*, **35**, 5054 (1941).

[15] E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, **1936**, 775.

Both induced and permanent magnetic moments may be present in a molecule. The presence of a permanent moment, due to unpaired electrons, or an odd number of electrons, leads to molecular paramagnetism.

The effective moment is given[16] by $\mu_{eff} = \sqrt{n(n+2)}$, in which n is the number of unpaired electrons. If this moment is known, or measurable, it becomes possible to compute the number of paired and unpaired electrons in the complex. If the number of electrons used in forming covalent bonds is known, the nature of the orbitals involved, and hence the spatial configuration, may be determined. The structure is square (planar) if all the s orbitals, all the p orbitals of a given level, and one d orbital are involved. The structure is tetrahedral when all s, all p orbitals of a given level, and three or more d orbitals are involved.

These criteria have been applied to the results of magnetic measurements on various complexes, particularly those of nickel. The complexes of quadricovalent nickel are easily classified as planar (square) or tetrahedral, depending on whether they are paramagnetic or diamagnetic. The divalent nickel ion has two unpaired $3d$ electrons and consequently is paramagnetic. If these are undisturbed, as in the formation of a tetrahedral complex involving ionic bonds, or covalent bonds with the $4s$ and $4p$ orbitals, the magnetic moment is unchanged. The moment is reduced to zero, however, upon utilization of the d orbitals, in the formation of four (planar) dsp^2 bonds; thus the complex under such circumstances is diamagnetic. It should be noted, however, that not all quadricovalent nickel complexes are diamagnetic, although all planar ones are.[17]

Pauling[18] has shown that, for quadricovalent atoms in which electrons from the s and p orbitals of the outer level are used, the tetrahedral configuration is the stable one. In the case of the transition elements, a d electron may be used, whereupon the covalencies lie in a plane. As the d electrons are responsible for the magnetic moment, sharing of these reduces the moment, and the compound may become diamagnetic. With nickel, for example, the moment is reduced from about 2.83 Bohr magnetons to nearly zero.

The nickel complexes listed in Table VI are all diamagnetic, hence planar in structure. The complexes of quadricovalent palladium and platinum are also diamagnetic and, therefore, planar. There is ap-

[16] P. W. Selwood, *Magnetochemistry*. Interscience, New York, 1943, p. 144.
[17] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 475 (1941).
[18] L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931).

TABLE VI

Configurations of Some Organometallic Complexes

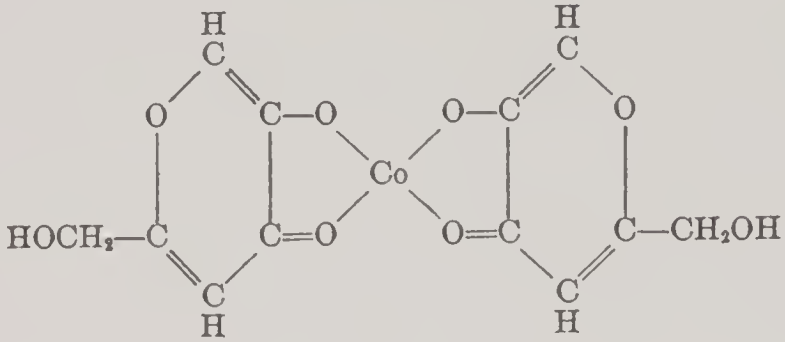
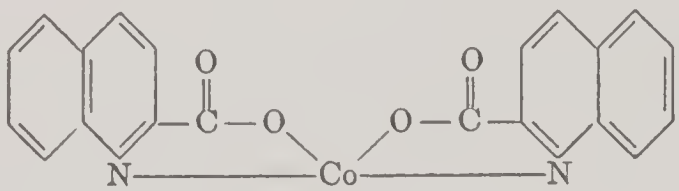
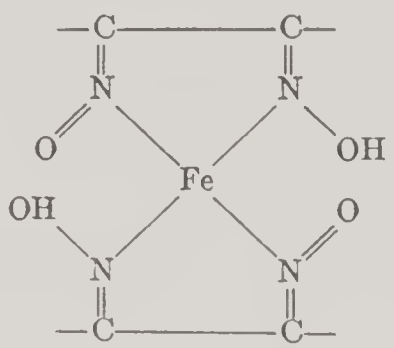
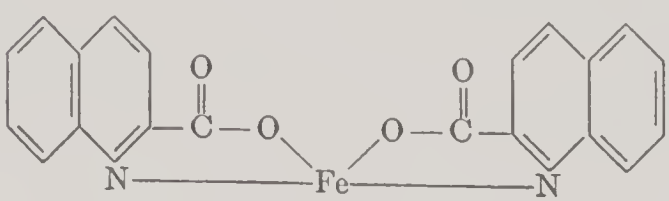
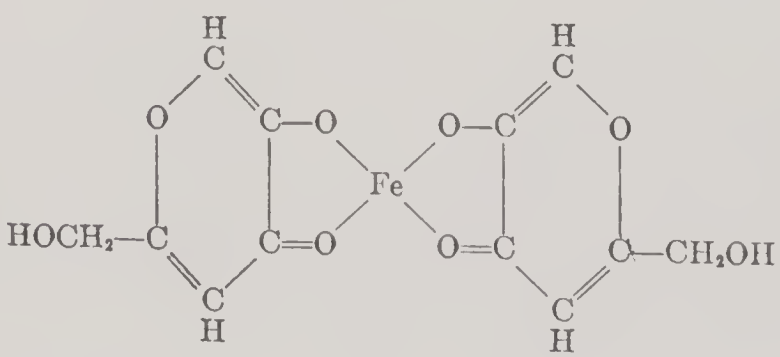
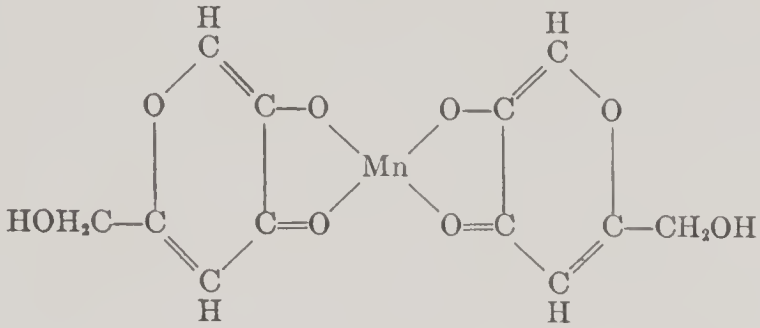
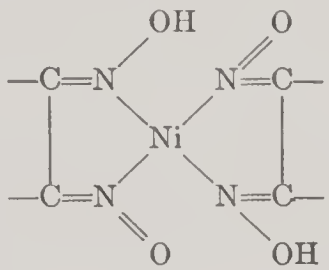
Compound	Formula	Structure
Cobalt kojate[a]		Tetrahedral
Cobalt quinaldate[b]		Tetrahedral
Ferrous glyoximes[c]		Planar
Ferrous quinaldate[d]		Tetrahedral
Ferrous kojate[a]		Tetrahedral

TABLE VI (*continued*)

Compound	Formula	Structure
Manganous kojate[a]		Tetrahedral
Nickel glyoximes[e]		All planar

[a] J. W. Wiley, G. N. Tyson, Jr., and J. S. Steller, *J. Am. Chem. Soc.*, **64**, 963 (1942).
[b] N. K. Dutt, *J. Indian Chem. Soc.*, **14**, 572 (1937).
[c] L. Cambi and A. Cagnasso, *Gazz. chim. ital.*, **64**, 772 (1934).
[d] L. Cambi and L. Szego, *Ber.*, **64**, 2591 (1931).
[e] H. J. Cavell and S. Sugden, *J. Chem. Soc.*, **1935**, 621.

parently no relation between color and configuration, although the diamagnetic nickel complexes are often bright red. The other compounds listed in Table VI find application, or possible application, in analytical work.

It has been pointed out that ferrous complexes containing the symmetrical group —N=C—C=N— are predominately diamagnetic, while those containing the unsymmetrical group —N=C—C=O are likely to be paramagnetic.

E. Summary

The coordination complexes used by the analyst are for the most part typical covalent compounds, with corresponding physical properties: they are slightly soluble in water, but soluble in nonpolar solvents, and are fairly easily volatilized or decomposed thermally. Their colors, often intense, are determined primarily by the resonance conditions within the organic portion of the molecule. Ample evidence exists to indicate a square or tetrahedral structure for a number of the complexes used in gravimetric analysis.

CHAPTER III

Separations by Means of Organic Reagents

As the majority of organic reagents in use are selective but not highly specific, the problem of making quantitative separations by means of organic reagents is of great interest. The general theoretical background of how such separations may be made is treated in this chapter.

The following methods of separation are commonly used in analytical chemistry: (*1*) extraction, (*2*) precipitation, (*3*) vaporization, and (*4*) adsorption. Of these only (*1*) and (*2*) have found use in connection with organic reagent work, although (*3*) and (*4*) should by no means be excluded from consideration. Distillation or sublimation at low pressures are techniques that might well afford a means for separating chelate compounds of the type in which the analyst is interested, and distinct advantages of such methods are conceivable. In this connection, attention might be given to the acetylacetonates which are relatively volatile and have considerable stability toward thermal decomposition. Adsorption might also serve to assist in making separations; here the technique could consist in passing a solution of the chelates in some nonpolar solvent through an adsorption column of the chromatographic type. Apparently no systematic studies of either of these techniques as analytical tools have been made, but the field seems well worth attention.

In the following sections the theory of separation by extraction and by precipitation will be given in detail.

Separations by Solvent Extraction

Extraction methods have proved very useful for the separation of an organometallic complex, or group of complexes, from aqueous solution by means of an immiscible solvent in which the chelate is soluble. Examples may be found in the extraction of metallic cupferrides with ether, of nickel dimethylglyoxime with chloroform, and of the

hydroxyquinolates and dithizonates with carbon tetrachloride or chloroform. Doubtless many other cases are known.

Recognition of the fact that the hydrogen ion concentration of the solution plays an important part in the extraction has been given in the cases of the hydroxyquinolates[1] and the dithizonates.[2] The range of *p*H over which extraction could be made complete was found to be rather narrow in the case of some hydroxyquinolates, with marked decreases at both high and very low *p*H values. Somewhat similar conditions exist for the dithizonates, with extraction starting rather abruptly at a definite *p*H.

A quantitative treatment of the extraction phenomena in the case of the dithizonates has been given by Kolthoff and Sandell.[3] They have given an equation relating the extraction coefficient of a metallic dithizonate (zinc), the *p*H of the aqueous solution being extracted, and the concentration of the chloroform solution of dithizone used to make the extraction. The relation is shown to be valid for the extraction of zinc with dithizone, and would certainly be expected to hold for other dithizonates. In fact, there is no reason to expect that the general approach would not apply to the extraction of other chelate compounds, such as the hydroxyquinolates, anthranilates, quinaldates, etc., among which there is general similarity of properties.

The reaction of a divalent metallic ion with dithizone (HDz, $C_6H_5N{=}N{-}\underset{\underset{S}{\|}}{C}{-}NH{-}NHC_6H_5$) in water is written as:

$$M^{++} + 2\,HDz \rightleftharpoons MDz_2 + 2\,H^+ \tag{1}$$

The "equilibrium constant" for this reaction is:

$$K = \frac{[H^+]_w^2[MDz_2]_w}{[HDz]_w^2[M^{++}]_w} \tag{2}$$

The distribution coefficients for dithizone and complex between water and the organic solvent are written as:

$$D_{HDz} = \frac{[HDz]_w}{[HDz]_o} \tag{3}$$

and:

$$D_{MDz_2} = \frac{[MDz_2]_w}{[MDz_2]_o} \tag{4}$$

[1] T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 346 (1943).
[2] L. P. Biefeld and T. M. Patrick, *ibid.*, **14**, 275 (1942).
[3] I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **63**, 1906 (1941).

The quantities $[HDz]_w$ and $[MDz_2]_w$ appearing in the equilibrium constant (2) may be expressed in terms of appropriate quantities from (3) and (4); the equilibrium constant thus becomes:

$$K = \frac{[MDz_2]_o[H^+]_w^2}{[M^{++}]_w[HDz]_o^2} = K' \frac{D_{HDz}^2}{D_{MDz_2}} \tag{5}$$

Now $\frac{[MDz_2]_o}{[M^{++}]_w}$ is the experimentally observed distribution coefficient, and it follows that:

$$\frac{[MDz_2]_o}{[M^{++}]_w} = K \frac{[HDz]_o^2}{[H^+]_w^2} \tag{6}$$

in which molar concentrations replace activities, for the solutions are generally very dilute.

This means that the extractability of the metallic ion M^{++} at a given *p*H increases as the square of the excess dithizone in the organic layer; also that, with a constant excess of dithizone, the extractability is inversely proportional to the square of the hydrogen ion concentration. The amount of metal extracted, then, is seen to be a sensitive function of both quantities.

It has been assumed in the preceding derivations that the metallic ion is present as the normal, aquated ion. If the *p*H of the system should be high enough for appreciable hydrolysis to occur, then appropriate modifications must be made. The hydrolysis constants corresponding to the reactions:

$$M^{++} + H_2O \rightleftarrows M(OH)^+ + H^+ \tag{7}$$

and:

$$M^{++} + 2\,H_2O \rightleftarrows M(OH)_2 + 2\,H^+ \tag{8}$$

are:

$$K_{1_{hyd}} = \frac{[M(OH)^+][H^+]}{[M^{++}]} \tag{9}$$

$$K_{2_{hyd}} = \frac{[M(OH)_2][H^+]^2}{[M^{++}]} \tag{10}$$

The total concentration of metallic ion [M] in solution is given by:

$$[M] = [M^{++}] + [M(OH)^+] + [M(OH)_2] \tag{11}$$

Introducing values from (9) and (10):

$$[M^{++}] = M\left\{\frac{[H^+]^2}{[H^+]^2 + K_{1_{hyd}}[H^+] + K_{2_{hyd}}}\right\} \tag{12}$$

Now if (12) is substituted in (6), it follows that:

$$\frac{[MDz_2]_o}{[M]_w} = K\frac{[HDz]_o^2}{\{[H^+]_w^2 + K_{1_{hyd}}[H^+] + K_{2_{hyd}}\}} \tag{13}$$

It is readily seen that when $K_{1_{hyd}}[H^+]_w + K_{2_{hyd}}$ is small compared to $[H^+]^2$, equation (13) reduces to the simpler form (6). When the metal is present entirely as hydroxide, then:

$$\frac{[MDz_2]_o}{[M]_w} = K\frac{[HDz]_o^2}{K_{2_{hyd}}} \tag{14}$$

which means that the extraction is independent of the *p*H of the aqueous layer.

As for practical applications, it is seen that if the K values [equation (6)] for the different metals are known one could set up conditions of *p*H and reagent concentration that would enable separation to be made. The lack of data on these constants currently hampers the full exploitation of this promising field.

Separations by Precipitation

Precipitation methods employing organic reagents are common and considerable interest attaches to the problem of making these precipitations selective. For a particular element, to be precipitated in the presence of other, potentially interfering elements, selectivity may be achieved in either of two ways (in lieu of having a specific reagent): (*1*) by using an agent to form a complex, slightly dissociated ion with the foreign elements, thus rendering their precipitation impossible under the conditions used; or (*2*) by controlling the *p*H of the solution. Use of the former method is by no means confined to analysis with organic reagents, and many examples from all branches of analytical chemistry could be cited. The use of organic hydroxy acids to retain iron(III) in solution at high *p*H values, the use of cyanide ion to complex the transition elements, as well as many heavier elements such as mercury and silver, and the use of thiourea to form complexes with mercury and silver (p. 254) are isolated, though typical examples. Based on the fact that the dissociation of the complex ion is insufficient to permit formation of an insoluble compound, it is clear that successful use of such agents depends on an accurate knowledge of the instability constants of the complex ions, as well as the solubility products of the insoluble salts that would form.

The influence of the hydrogen ion concentration on precipitations

and separations with organic reagents can be described in a reasonably quantitative manner. The influence of the hydrogen ion concentration on the completeness of precipitation was recognized early, although initially the hydrogen ion concentration of the solution required for precipitation was described somewhat loosely as "acid," "neutral," or "alkaline." In many cases, particularly the determination of a single substance, this was adequate. Likewise, this description was sufficiently accurate for strongly acidic solutions (*e.g.*, the solution used in the precipitation of palladium by dimethylglyoxime) and for strongly ammoniacal solutions (*e.g.*, the solution used in the precipitation of nickel by the same reagent), provided that no interfering ions were present.

Unfortunately, most of the organic reagents available are not as selective as dimethylglyoxime. A useful reagent such as 8-hydroxyquinoline may precipitate several ions in "acidic" solution, and many more in "neutral" or "alkaline" solution. Nor can the conditions be described adequately by the terms, "weakly acid," "strongly acid," etc.; therefore, the acidity conditions necessary for precipitation are now expressed precisely in terms of *p*H.

Some of the first work along this line was done by Fleck and Ward, and by Goto. Using known amounts of metallic ion and precipitant, they determined the *p*H (with glass or hydrogen electrodes) at which incipient precipitation occurs, and also the point at which quantitative precipitation of the element is attained. Some data of these authors, shown in Table VII, suggest possible separations. For example, cadmium precipitates completely at *p*H 5.66 to 14.58; for tungsten, the range is 4.95 to 5.65; and for uranium, 4.1 to 8.8. Thus, it should be possible to separate tungsten from cadmium, uranium from cadmium, and tungsten and (or) uranium from molybdenum, which precipitates completely at *p*H 3.60 to 7.33. In order to carry out these separations, one might first remove the precipitate formed at the lower *p*H, and then increase the *p*H for the precipitation of the second element. Other separations should be possible according to Goto's data, for example, the separation of iron and copper (which were found to precipitate completely at *p*H 2.7 to 2.8) from other elements, *e.g.*, magnesium, calcium, lead, cadmium, and manganese (which do not precipitate until higher *p*H values are attained).

A systematic study of separations with 8-hydroxyquinoline was made by Moyer and Remington.[4] From data obtained on the separa-

[4] H. V. Moyer and W. J. Remington, *Ind. Eng. Chem., Anal. Ed.*, **10**, 212 (1938).

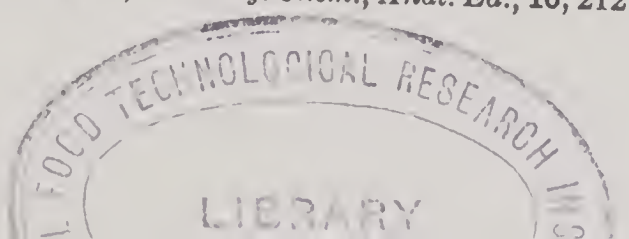

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TABLE VII

*p*H Range for Complete Precipitation

Ion	Goto[a]	Fleck and Ward[b]	Others
Aluminum	4.2 to 9.8		
Bismuth	4.8 to 10.5		
Cadmium	5.4 and higher	5.66 to 14.5	
Calcium	9.2 and higher		
Cobalt	4.2 to 11.6	4.33 to 14.5	
Copper(II)	2.7 and higher	5.33 to 14.5	
Iron(III)	2.8 to 11.2		
Lead	8.4 to 12.3		9.3 to 9.4[c]
Magnesium	8.2 and higher		
Manganese(II)	5.9 to 10		
Molybdenum(VI)	3.3 to 7.6	3.60 to 7.33	
Nickel	4.6 to 10	4.33 to 14.5	
Thorium(IV)	4.4 to 8.8		
Titanium(III)	4.8 to 8.6		
Tungsten(VI)		4.95 to 5.65	3.3 to 3.5[d]
Uranium(VI)	4.1 to 8.8		
Vanadium(V)	2.7 to 6.1		
Zinc	4.4 and higher	4.58 to 13.4	

[a] H. Goto, *J. Chem. Soc. Japan*, **54**, 725 (1933); **56**, 314 (1935). *Sci. Repts. Tohoku Imp. Univ.*, **26**, 391 (1937); **26**, 418 (1938).
[b] H. R. Fleck and A. M. Ward, *Analyst*, **58**, 388 (1933); **62**, 378 (1937).
[c] V. Marsson and L. W. Haase, *Chem. Ztg.*, **52**, 993 (1928).
[d] S. Halberstadt, *Compt. rend.*, **205**, 987 (1937).

tion of zinc and magnesium, and of iron and aluminum, they concluded that even more careful control of the *p*H is necessary than had been indicated by earlier observations made on solutions of single metals. When zinc was precipitated with 8-hydroxyquinoline in the presence of magnesium, a partial precipitation of magnesium begins at *p*H 5.5. Under the same conditions, precipitation of magnesium alone begins at *p*H 7.5. In the case of iron and aluminum, good separations are obtained only in the *p*H range 3.5 to 4.0 under the experimental conditions. The authors were able to show that the coprecipitation of magnesium on zinc hydroxyquinolate, at *p*H 5.95, and the coprecipitation of aluminum on ferric hydroxyquinolate, at *p*H 4.10, both increase in accordance with an adsorption isotherm. They concluded that the coprecipitation was actually an adsorption on the surface of the precipitate.

Biefeld and Howe[5] made a similar study with salicylaldoxime on the separation of copper and nickel, and copper and iron. Under their conditions, they found that the copper complex is quantitatively pre-

[5] L. P. Biefeld and D. E. Howe, *Ind. Eng. Chem., Anal. Ed.*, **11**, 251 (1939).

cipitated at *p*H 2.6, whereas the nickel complex begins to precipitate at *p*H 3.3. The *p*H range 2.6 to 3.1, suitable for the separation of copper and nickel, is not appreciably different from that which had been predicted from results obtained with pure solutions. Even at *p*H 3.1 observations, made over a wide range of nickel concentrations, showed that there is little entrainment of the nickel complex by the copper complex. Furthermore, the small amount coprecipitated increases with increasing nickel concentration, all other factors remaining constant. In the case of iron, the entrainment on the copper complex at *p*H 2.8 increases with both iron concentration and *p*H; thus, the authors concluded that adsorption alone is not responsible for the entrainment.

It will be noted that most of the organic reagents whose function is sensitive to *p*H are weak acids or bases, or both. Thus, 8-hydroxyquinoline is a weak acid ($K_a = 4 \times 10^{-11}$) *and* a weak base ($K_b = 1 \times 10^{-10}$), salicylaldoxime a weak acid ($K_a = 10^{-5}$) and a weak base ($K_b = 10^{-12}$), quinaldic acid a weak acid ($K_a = 1.2 \times 10^{-5}$), and so on. If we designate the general monobasic precipitant of this type as HX, then the precipitation reaction may be written as:

$$M^{n+} + n\,HX \rightleftharpoons MX_n + n\,H^+ \qquad (15)$$

for a positive ion M of charge *n*. The effect of acid on this equilibrium is immediately apparent. If the anion X^- is taken to include HS^-, OH^-, $HC_2O_4^-$, HCO_3^-, and $HCrO_4^-$, as well as the organic anions, it is recognized that many common precipitations are influenced by the hydrogen ion exactly as are precipitations with organic reagents. Sulfide precipitations, the precipitation of calcium oxalate, barium and strontium chromates, etc., are classical cases.

From this it is evident that the solubility of an organometallic complex and, thus, completeness of its precipitation depend on the hydrogen ion concentration, and on the concentration of precipitant, HX, as well as on the concentration of metallic ion. The latter factors were overlooked to some extent by the early workers in the field.

A. Precipitation by a Monobasic Acid

If the formation of a precipitate is considered in Equation (15), then the precipitate will redissolve in accordance with (16):

$$MX_n \rightleftharpoons M^{n+} + n\,X^- \qquad (16)$$

or better, as X^- is the anion of a weak electrolyte, in accordance with:

$$MX_n + n\,H^+ \rightleftharpoons M^{n+} + n\,HX \qquad (17)$$

In the case of salts of divalent metal ions, MX_2, some complexes dissolve via Equation (18)[6]:

$$MX_2 + H^+ \rightleftharpoons MX^+ + HX \tag{18}$$

The solubility product constant, S, of the insoluble salt is:

$$S_{MX_n} = (f_{M^{n+}}C_{M^{n+}})(f_{X^-}C_{X^-})^n \tag{19}$$

where f is the activity coefficient and C is the molar concentration. The activity of X^- is obtained from the ionization constant of the weak electrolyte at the temperature in question:

$$K_{HX} = \frac{(f_{H^+}C_{H^+})(f_{X^-}C_{X^-})}{(f_{HX}C_{HX})} \tag{20}$$

$$(f_{X^-}C_{X^-}) = \frac{K_{HX}(f_{HX}C_{HX})}{(f_{H^+}C_{H^+})} \tag{21}$$

If we combine Equations (19) and (21), the solubility product constant becomes:

$$S_{MX_n} = \frac{(f_{M^{n+}}C_{M^{n+}})\{(K_{HX})(f_{HX}C_{HX})\}^n}{(f_{H^+}C_{H^+})^n} \tag{22}$$

Now the changes in ion concentration during precipitation may be considered. If the fraction of metallic ion precipitated is α, then at any point between incipient and complete precipitation the activity of metallic ion will be given by:

$$(C_{M^{n+}})(f_{M^{n+}}) = (C^0_{M^{n+}}f_{M^{n+}})(1 - \alpha) \tag{23}$$

in which $C^0_{M^{n+}}$ is the initial concentration of metallic ion in solution before start of precipitation.

The corresponding amount of precipitant, HX, in equilibrium at any point, will be given by:

$$(f_{HX}C_{HX}) = (f_{HX}C^0_{HX}) - n\alpha(C^0_{M^{n+}}f^0_{M^{n+}}) \tag{24}$$

where C^0_{HX} is the initial concentration of HX in solution. If Equations (22), (23), and (24) are combined, the hydrogen ion activity corresponding to any fraction α of precipitation is:

$$(f_{H^+}C_{H^+}) = \frac{\sqrt[n]{(C_{M^{n+}}f_{M^{n+}})(1-\alpha)}(K_{HX})\{(f_{HX}C^0_{HX}) - n\alpha(f_{M^{n+}}C^0_{M^{n+}})\}}{\sqrt[n]{S_{MX_n}}} \tag{25}$$

For solutions as dilute as those generally encountered in practical analyses (10^{-2} to 10^{-3} M or less) activity coefficients are taken as unity at room temperature. Equation (25) then becomes:

[6] W. D. Treadwell and A. Ammann, *Helv. Chim. Acta*, **21**, 1249 (1938).

$$C_{H^+} = \frac{\sqrt[n]{C^0_{M^{n+}}(1-\alpha)}\ (K'_{HX})\{C^0_{HX} - n\alpha C_{M^{n+}}\}}{\sqrt[n]{S'_{MX_n}}} \qquad (26)$$

in which the primed constants are no longer the thermodynamic quantities.

Thus, if the solubility product constant for a particular salt is known, the hydrogen ion concentration needed for any degree of precipitation of that salt may be calculated, provided that the other quantities are known. The curve of *p*H *vs.* per cent precipitation (shown in Fig. 1) given by this function resembles closely the curves

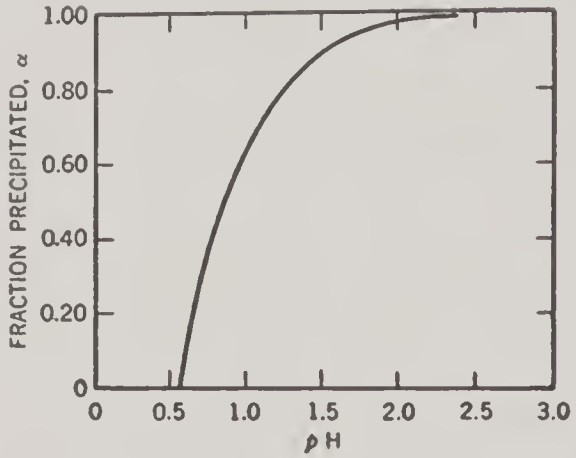
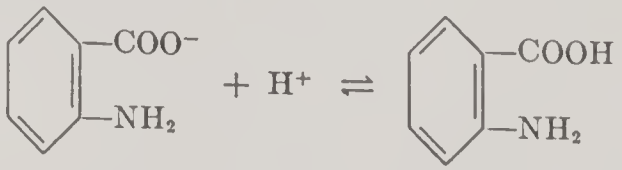


Fig. 1. Precipitation of 10^{-3} *M* Cu^{++} by 3×10^{-3} *M* quinaldic acid.

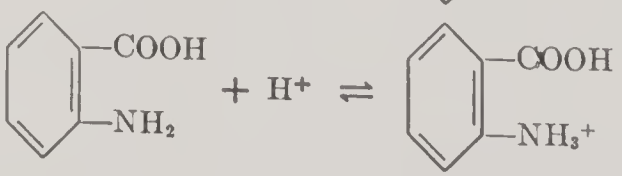
reported by Goto, Moyer and Remington, and Biefeld and Howe. The curve is similar also in shape to the curve of *p*H *vs.* per cent ionization of a weak acid or base, as would be expected if precipitation depended on the supply of X^- ions in solution.

B. Precipitation by a Dipolar Ion

Some organic precipitants, like anthranilic acid and, to a lesser degree, 8-hydroxyquinoline, are capable of existing as dipolar ions. Thus, for anthranilic acid, we may write:



(27)



(28)

In general, for an acid of this type we may write:

$$H_2X^+ \rightleftharpoons HX^{\pm} + H^+ \tag{29}$$

$$HX^{\pm} \rightleftharpoons H^+ + X^- \tag{30}$$

from which the dissociation constant of the ammonium ion acid, H_2X^+, is:

$$K_1 = \frac{(f_{HX^{\pm}}C_{HX^{\pm}})(f_{H^+}C_{H^+})}{(f_{H_2X^+}C_{H_2X^+})} \tag{31}$$

and the dissociation constant of the carboxylic acid, $HX^{\pm}$, is:

$$K_2 = \frac{(f_{H^+}C_{H^+})(f_{H^-}C_{H^-})}{(f_{HX^{\pm}}C_{HX^{\pm}})} \tag{32}$$

The solubility product constant of a salt of this acid will be the same as given previously (Eq. 19). Solving Equation (19) for $f_{X^-}C_{X^-}$, we have:

$$(f_{X^-}C_{X^-}) = \sqrt[n]{\frac{(S_{MX_n})}{(f_{M^{n+}}C_{M^{n+}})}} \tag{33}$$

Solution of (32) for the hydrogen ion activity gives:

$$(f_{H^+}C_{H^+}) = \frac{K_2(f_{HX^{\pm}}C_{HX^{\pm}})}{(f_{X^-}C_{X^-})} \tag{34}$$

Combining (33) and (34), we have:

$$(f_{H^+}C_{H^+}) = K_2\sqrt[n]{\frac{(f_{M^{n+}}C_{M^{n+}})}{S_{MX_n}}}\,(f_{HX^{\pm}}C_{HX^{\pm}}) \tag{35}$$

The activity of the neutral precipitant, $HX^{\pm}$, is given by:

$$\begin{aligned}(f_{HX^{\pm}}C_{HX^{\pm}}) = {} & (f_{HX_0^{\pm}}C_{HX_0^{\pm}}) - (f_{X^-}C_{X^-}) \\ & - n\{(f_{M_0^{n+}}C_{M_0^{n+}}) - (f_{M^{n+}}C_{M^{n+}})\} - (f_{H_2X^+}C_{H_2X^+})\end{aligned} \tag{36}$$

in which $C_{HX_0^{\pm}}$ denotes the initial stoichiometric amount of precipitant, and $C_{M_0^{n+}}$ the initial concentration of metallic ion being precipitated.

If Equations (31), (33), and (36) are combined, we have:

$$\begin{aligned}(f_{HX^{\pm}}C_{HX^{\pm}}) = {} & (f_{HX_0^{\pm}}C_{HX_0^{\pm}}) - \sqrt[n]{\frac{S_{MX_n}}{(f_{M^{n+}}C_{M^{n+}})}} \\ & - n\{(f_{M_0^{n+}}C_{M_0^{n+}}) - (f_{M^{n+}}C_{M^{n+}})\} - \frac{(f_{HX^{\pm}}C_{HX^{\pm}})(f_{H^+}C_{H^+})}{K_1}\end{aligned} \tag{37}$$

Upon solving Equation (37) for the activity of HX, we have.

$$(f_{HX\pm}C_{HX\pm}) = \frac{(f_{HX_0^{\pm}}C_{HX_0^{\pm}}) - n\{(f_{M_0^{n+}}C_{M_0^{n+}}) - (f_{M^{n+}}C_{M^{n+}})\} - \sqrt[n]{\dfrac{S_{MX_n}}{(f_{M^{n+}}C_{M^{n+}})}}}{1 + \dfrac{(f_{H^+}C_{H^+})}{K_1}} \quad (38)$$

Combination of Equations (35) and (38) gives:

$$(f_{H^+}C_{H^+}) = K_2\sqrt[n]{\frac{(f_{M^{n+}}C_{M^{n+}})}{S_{MX_n}}} \left\{\frac{(f_{HX_0^{\pm}}C_{HX_0^{\pm}}) - n\{(f_{M_0^{n+}}C_{M_0^{n+}}) - (f_{M^{n+}}C_{M^{n+}})\} - \sqrt[n]{\dfrac{S_{MX_n}}{(f_{M^{n+}}C_{M^{n+}})}}}{1 + \dfrac{(f_{H^+}C_{H^+})}{K_1}}\right\} \quad (39)$$

Now at any point on the *p*H *vs.* fraction precipitated curve:

$$(f_{M^{n+}}C_{M^{n+}}) = (f_{M_0^{n+}}C_{M_0^{n+}})(1 - \alpha) \quad (40)$$

Equations (39) and (40) may be combined, and when (39) is rearranged to facilitate solution for H^+, we have:

$$(f_{H^+}C_{H^+})^2 + K_1(f_{H^+}C_{H^+}) - \frac{K_1K_2}{\sqrt[n]{S_{MX_n}}}\sqrt[n]{(f_{M_0^{n+}}C_{M_0^{n+}})}\sqrt[n]{1 - \alpha}$$

$$\left\{(f_{HX_0^{\pm}}C_{HX_0^{\pm}}) - n\alpha(f_{M_0^{n+}}C_{M_0^{n+}}) - \sqrt[n]{\frac{S_{MX_n}}{(f_{M_0^{n+}}C_{M_0^{n+}})(1 - \alpha)}}\right\} = 0 \quad (41)$$

Generally the last term in Equation (41), which corrects for the amount of HX dissolved from the precipitate, may be neglected. If the last term of the remaining equation is called β, then:

$$(f_{H^+}C_{H^+})^2 + K_1(f_{H^+}C_{H^+}) - \beta = 0 \quad (42)$$

and:

$$(f_{H^+}C_{H^+}) = [(K_2/2)^2 + \beta]^{1/2} - K_2/2 \quad (43)$$

Activity coefficients for the ions H^+, M^{n+}, X^-, and H_2X^+ may be obtained from the extended Debye-Hückel equation, if required. These have the form:

$$\log f = A\sqrt{\mu} + C\mu \quad (44)$$

The activity coefficient of the dipolar ion, HX^+, is (limiting value):

$$-\log f = \frac{A}{D^2T^2} \cdot \frac{R^2}{a}\mu \quad (45)$$

in which R is the distance between charges in the dipolar ion, a is the

mean distance of closest approach of other ions to this ion, D is the dielectric constant of the medium of ionic strength μ at the temperature T, and A is a constant whose value can be derived theoretically.

At the concentrations encountered in most analytical precipitations, the ionic strengths are low, and the activity coefficients approach unity. Furthermore, at the present time the precision of data on solubility products is not sufficient to warrant use of other than molarities in making the calculations.

Note that the values of ionization constants, K_1 and K_2, of the dipolar ion must be known when solving Equation (41). A complete and well-edited assemblage of such data is given by Cohen and Edsall.[7] If K_1 (dissociation constant of the ammonium ion acid) is large, *i.e.*, approaches unity, Equation (41) takes on the same form as the equation for a simple acid precipitation with HX (see Eqs. 25 and 26). Even with a precipitant of the H_2X^+ type, the importance of the zwitterion becomes less as the *p*H increases; this means that the term $K_1(f_{H+}C_{H+})$ in Equation (41) becomes small in comparison with $(f_{H+}C_{H+})^2$, and the calculation reduces to the same type as for Equations (25) and (26).

In many cases the insoluble organometallic complex may be dissolved at high *p*H by ammonia or sodium hydroxide, or metathesized by sodium hydroxide. In the first instance the *p*H *vs.* per cent precipitation curves drop at high *p*H, as shown by Goto,[8] and as verified by work in the author's laboratory. If the precipitate dissolves with the formation of an ammine complex (silver, copper, nickel, cobalt, zinc, cadmium, etc.), the *p*H can be estimated as follows. From Equation (19):

$$(f_{M^{n+}}C_{M^{n+}}) = \frac{S_{MX_n}}{(f_{X^-}C_{X^-})^n} \tag{46}$$

The instability constant of the ammine is:

$$K_{inst.} = \frac{(f_{M^{n+}}C_{M^{n+}})(f_{NH_3}C_{NH_3})^{2n}}{(f_{M(NH_3)_{2n}^{n+}}C_{M(NH_3)_{2n}^{n+}})} \tag{47}$$

At the point where the precipitate just dissolves:

$$(f_{NH_3}C_{NH_3}) = \sqrt[2n]{\frac{(K_{inst.})(f_{M(NH_3)_{2n}^{n+}}C_{M(NH_3)_{2n}^{n+}})(f_{X^-}C_{X^-})^n}{S_{MX_n}}} \tag{48}$$

[7] E. J. Cohen and J. T. Edsall, *Proteins, Amino Acids, and Peptides*. Reinhold, New York, 1943, Chapter IV.

[8] H. Goto, *J. Chem. Soc. Japan*, **54**, 725 (1933); **56**, 314 (1935); *Sci. Repts. Tôhoku Imp. Univ.*, **26**, 391 (1937); **26**, 418 (1938).

The amount of ammonium hydroxide required to produce this amount of ammonia, and the corresponding *p*H, can be calculated from the ionization equilibrium of ammonia. For 0.01 *M* copper quinaldate, the *p*H is about 11.3, a value that is also found experimentally.

If the precipitate dissolves in sodium hydroxide, similar reasoning may be applied; the instability or ionization constant of the complex hydroxide anion then replaces the instability constant of the metal ammine in Equation (48).

Simple metathesis of an organometallic complex occurs in few cases in practical work. Examples which might be cited are the treatment of iron cupferride precipitates with base to produce ferric hydroxide (see page 136), and the treatment of copper quinaldate with sodium hydroxide during the recovery of quinaldic acid from precipitates. In general, the extent of the metathesis will depend on the relative solubilities of the complex and the metallic hydroxide.

C. Methods of Evaluating the Solubility Products

Two distinctly different methods have been employed to obtain the solubility product constants for organometallic compounds of the type used in gravimetric and volumetric analysis. The classical method used by Treadwell and Ammann[6] consists in saturating a solution, at given temperature, pressure, and *p*H, with the insoluble salt. The content of the saturated solution, determined in some manner, gives the equilibrium solubility of the salt and thus the solubility product constant. Some values obtained in this manner are given in Table VIII (page 71).

The second method makes use of Equation (25) to determine the solubility product constant. The *p*H of a solution containing known concentrations of precipitant and metallic ion is adjusted until precipitation begins. The mixture is then allowed to stand (at constant temperature) for a given period of time; then the precipitate is filtered, washed, dried, and weighed. From the known amount of metal taken and the amount of metal precipitated the fraction, α, can be calculated. Thus, Equation (25) can be solved for the solubility product constant. Some values obtained by this method are given in Table XIV (page 96).

It is apparent that the two methods do not yield identical results, although, in many cases, the agreement is reasonably good as solubility measurements go. Since the conditions under which the latter

values were obtained are nearly identical with the conditions under which they are to be used, it seems justifiable to employ them in preference to the other data for the purposes to be described. As the reproducibility of the type of measurement used in the second method is good, there is no reason to believe that a set of such solubility products for various ions should not prove to be consistent, at least within itself.

Mention should be made here of the possibility of using the polarograph to determine the solubilities of slightly soluble organometallic complexes. The determination of very low concentrations of metallic ions may be carried out easily and accurately by this technique; hence, it should be adaptable to the analysis of saturated solutions of these insoluble compounds. The method has, indeed, been used to determine the solubility of magnesium hydroxyquinolate (see p. 181), and should work well with a host of other complexes.

D. Applications of the Solubility Product Data

It might be pointed out initially that many organometallic compounds of the type used in analytical work are of a degree of insolubility comparable with few other salts except hydroxides and sulfides. For example, the nickel and zinc hydroxyquinolates are about as soluble as the corresponding sulfides, while the cadmium, cobalt, and lead hydroxyquinolates are only slightly more soluble than the corresponding sulfides. The zinc and lead hydroxyquinolates are less soluble than the corresponding hydroxides. Thus, merely as a precipitating agent, without regard to any analytical procedure, the organic reagent may afford a more selective and complete removal of an ion than will any other reagent. The fact that the organic precipitant can be reclaimed in many cases (see page 91) might make reactions of this type interesting for industrial processes. Accurate knowledge of relative solubilities would be essential in the selection of a precipitant for such purposes.

A more immediate consequence, at least for analytical work, of the foregoing treatment of solubility, is the specification of exact conditions for precipitation. As mentioned earlier, much data on the "*p*H for precipitation" of various metals by organic precipitants has been assembled. It is now evident that, while these *p*H values may indeed be the *p*H values at which precipitation is quantitative under the conditions used, they are not the *p*H values at which precipitation

is quantitative under *all* concentrations of metallic ion and precipitant.

Inspection of Equations (25) and (41) (pages 54 and 57, respectively) shows how the minimum *p*H for quantitative precipitation may be found. If $\alpha = 0.999$ as taken for complete precipitation, Equation (25) becomes:

$$(f_{H^+}C_{H^+}) = \frac{\sqrt[n]{f_{M^{n+}}C_{M_0^{n+}}(0.001)}K_{HX}}{\sqrt[n]{S_{MX_n}}} \tag{49}$$

and β in Equation (41) becomes:

$$\beta = \frac{K_1K_2}{\sqrt[n]{S_{MX_n}}}\sqrt[n]{f_{M^{n+}}C^0_{M^{n+}}(0.001)}\{(f_{HX_0^{\pm}}C^0_{HX_0^{\pm}}) - 0.999\, n(f_{M_0^{n+}}C^0_{M^{n+}})\} \tag{50}$$

Thus, the minimum *p*H for quantitative precipitation depends on the concentrations of metal and precipitant, and on the ionization and solubility product constants in question.

The *p*H necessary to just *prevent* precipitation of an element may be calculated in a like manner. In this case, $\alpha = 0$, and Equation (25) becomes:

$$f_{H^+}C_{H^+} = \frac{\sqrt[n]{C^0_{M^{n+}}f_{M^{n+}}}}{\sqrt[n]{S_{MX_n}}}(K_{HX})(f_{HX}C^0_{HX}) \tag{51}$$

and β in Equation (41) becomes:

$$\beta = -\frac{K_1K_2}{\sqrt[n]{S_{MX_n}}}\sqrt[n]{f_{M^{n+}}C^0_{M^{n+}}}\{f_{HX^{\pm}}C^0_{HX^{\pm}}\} \tag{52}$$

It is immediately apparent that the *p*H range, over which a pair of ions of known concentrations can be separated, is determinable. First, on the basis of the solubility products of the insoluble salts, a concentration of reagent is chosen which will be sufficient to precipitate one or both of the ions present. Then, the minimum *p*H for quantitative precipitation of the less soluble salt is computed by Equation (49) or Equations (50) and (41). Next, the *p*H, required to just prevent precipitation of the more soluble salt is computed by Equation (51), or Equations (52) and (41), the decrease of reagent concentration caused by precipitation of the first element having been taken into account. The *p*H range for separation then would be $p\text{H}_{\alpha=0.999} - p\text{H}_{\alpha=0}$.

The *p*H value at which the less soluble element would be precipitated would be in the region:

$$p\mathrm{H} = \frac{p\mathrm{H}_{\alpha = 0.999} - p\mathrm{H}_{\alpha = 0}}{2} \qquad (53)$$

Obviously, better results will be obtained if only enough reagent is added to combine with the less soluble element.

There is not much information available on separations predicted in this manner. The results obtained in a few cases are summarized in Chapters VI and XVI. From these data and from other work done in the author's laboratory, it appears that, in the case of anthranilates and quinaldates, the range should be at least 2 *p*H units for a completely satisfactory separation. With a narrower range, precipitation of the more soluble salt tends to occur. This may be due either to adsorption (Moyer and Remington), or to nonequilibrium conditions—*i.e.*, concentration gradients, etc.—set up in the solution during precipitation. It would prove difficult to establish the mechanism of the precipitation in all instances.* It also appears that separations made at the lower end of the *p*H scale are more successful than those made higher, say at *p*H 3–5, where basic salt formation may be a complicating factor. In cases of coprecipitation. a single reprecipitation generally gives a clean separation.

The separations reported in Chapter VI (page 97) were made with an amount of reagent more than equivalent to both ions present. This naturally tends to favor precipitation of the more soluble element. The separations reported by Moyer and Remington,[4] and by Biefeld and Howe,[5] were made with an amount of reagent equivalent only to the element being precipitated, and, in these cases, the use of a narrow *p*H range apparently was not harmful. In general, then, it is preferable to use the minimum quantity of precipitant for each precipitation.

For a given pair of ions at a definite concentration, the *p*H range for separation will depend primarily on the concentrations and on the solubility products of the complexes. Variation in the amount of precipitant, if it is present in amounts equivalent to both ions, has relatively little effect on the range for separation. The operation of some

*It may well be that adsorption is an important factor, in the case of ions of the type MX^+ that remain in solution; they would be adsorbed by the precipitate of $M'X_2$, which probably would be of the same lattice type.

of these variables is shown in Figures 2 to 4. In the first of these, the *p*H range for precipitation of copper, zinc, and cadmium with quinaldic acid is shown. As the concentrations of ion and precipitant are identical in all instances, the displacement of the curves is the result

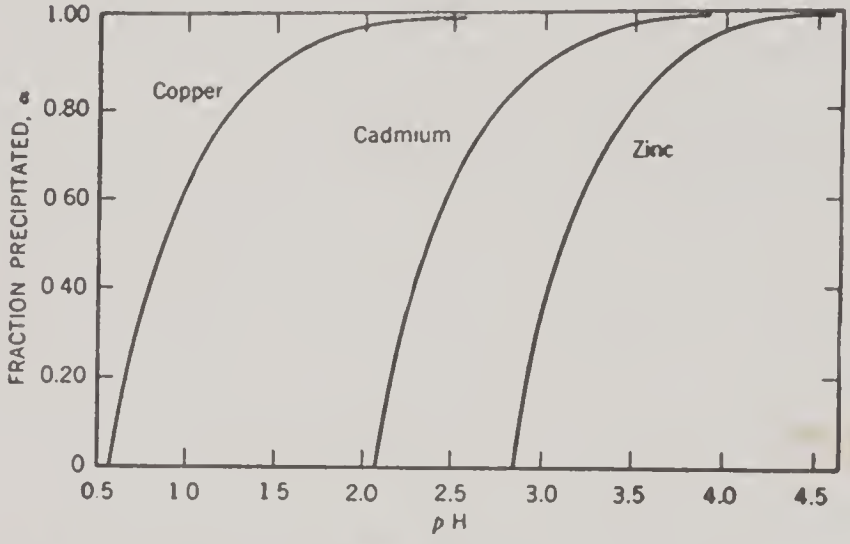


Fig. 2. Precipitation of 0.001 *M* Cu^{++}, Cd^{++}, and Zn^{++} by 0.003 *M* quinaldic acid.

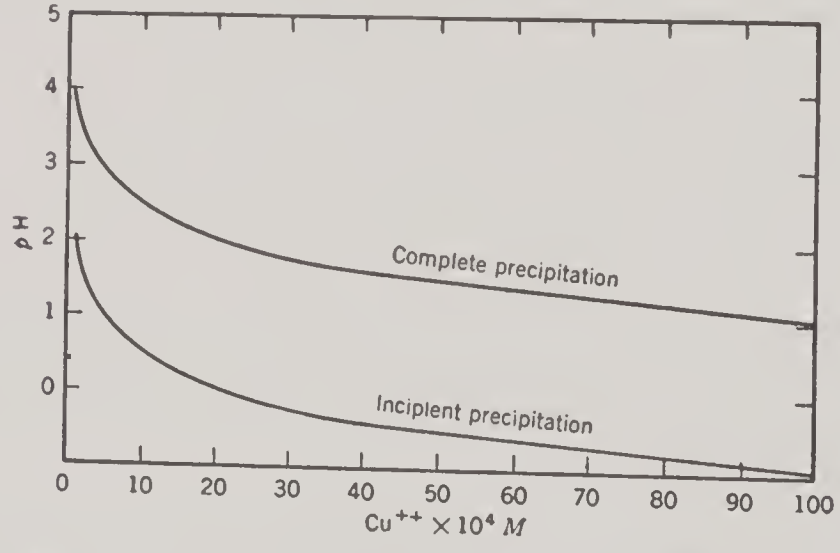


Fig. 3. Precipitation of copper by quinaldic acid at constant ratio (HX/M).

of differences in solubility products. Figure 3 shows the change in the *p*H required for incipient and complete precipitation as a function of the copper ion concentration; the precipitant is again quinaldic acid. In this case, the ratio of precipitant to metal is constant over the range of concentrations, and equals 3. The fourth figure gives, for a

constant concentration of copper (0.001 *M*), the changes in *p*H required for incipient and complete precipitation as a function of quinaldic acid concentration.

Throughout the preceding discussions, a knowledge of ionic concentrations has been assumed. While this is never true in an actual analysis, still there are many cases in which the concentration of the element to be precipitated can be estimated beforehand with reasonable accuracy, and thus the proper conditions for precipitation, arrived at. As noted earlier, in many cases in which a single ion is to be precipitated, a simpler specification of the *p*H needed for complete

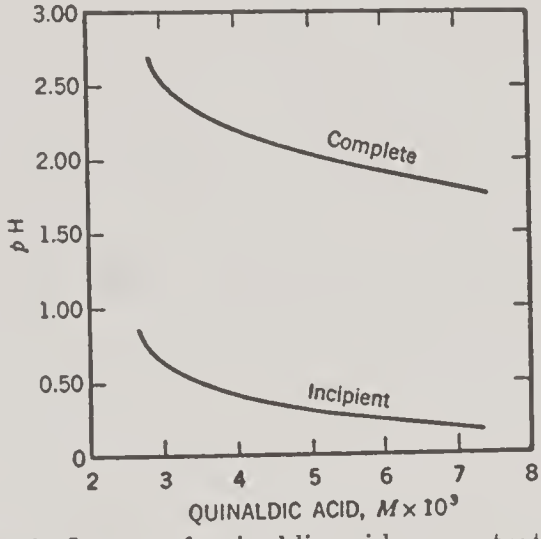


Fig. 4. Influence of quinaldic acid concentration on precipitation of 0.001 *M* Cu^{++}.

precipitation will suffice. In some instances the *p*H must not be too high, otherwise redissolution of the precipitate occurs. Hence, a safe guide to the proper conditions to use may be found in the methods of calculation outlined.

The point of view taken in the foregoing sections is reasonably consistent with published work of other authors. Moyer and Remington[4] reported an increased coprecipitation of magnesium on zinc hydroxyquinolate, and iron on aluminum hydroxyquinolate, with increasing magnesium and iron concentrations, at constant *p*H, and (presumably) with constant amount of precipitant. This is to be expected, as an increase of $C^0_{M^n}$ (Eq. 25, page 54) will cause an increase in α, all other factors remaining constant. Their finding that a constant amount is carried down after a certain concentration is reached may

well represent the maximum precipitation possible with the quantity of reagent used. The possibility of adsorption cannot be excluded, of course, although Biefeld and Howe[5] were able to show that very little entrainment of nickel by copper salicylaldoxime occurred over a wide range of concentrations, at constant *p*H. Apparently they were working well outside the range of precipitation of nickel salicylaldoxime.

E. Summary

General principles for precipitations and separations involving organic reagents can be set down, and it becomes possible to select the proper *p*H for a precipitation or separation. Concentrations of precipitant and metallic ion, as well as the solubility products of the insoluble salts, must be known approximately. Results obtained in a few cases are in good agreement with the theory. The principles apply only, so far, to precipitations with reagents that: (*1*) form salts of definite composition with metals, (*2*) form stable compounds that may be dried and weighed under ordinary conditions (although this is not strict requirement), and (*3*) are weak acids (or bases) with known ionization constants. Among such reagents are included anthranilic acid, quinaldic acid, 8-hydroxyquinoline, and salicylaldoxime.

CHAPTER IV

Theory of the Solubility of Salts with a Common Anion

In Chapter III the behavior of organic precipitants was described with particular reference to the conditions under which they combine with metallic ions. The key to the treatment discussed there consisted in knowing accurately the solubility products of the insoluble complexes. This naturally leads to the more fundamental question as to why these salts are insoluble *i.e.* what is inherent in the character of the salt-forming group that makes for an insoluble combination with a metallic ion, regardless of *p*H? A change in the *p*H merely alters the amount of reagent anion available for precipitation; the basic question concerns why the reagent anion causes precipitation.

Such answers as can be given must depend on analogy, and must follow an approach that is largely descriptive. It is not yet possible to predict the sort of molecule that would have to be built to combine with element X and no other element, much less to predict what the solubility of the resultant salt would be. On the basis of past experience, we can predict the types of grouping which are likely to combine with some of the commoner elements, but these are not *specific* combinations, and we do not know quantitatively what their solubilities will be. However, it is likely that we shall be able to make such predictions eventually.

A fundamental tudy of the solubility problem, in connection with some salts of the type considered in this book, has been given by Treadwell and Ammann.[1] They have outlined a theoretical treatment for the solubility of salts with a common anion, and have attempted predictions of relative solubility values on a more or less *a priori* basis. Their treatment of the solubility problem will be given in detail, not because it represents a solution to the solubility problem, but rather because it points directly to a way of handling such matters, and bears more or less directly on organometallic salts.

[1] W. D. Treadwell and A. Ammann, *Helv. Chim. Acta*, **21**, 1249 (1938).

Treadwell and Ammann measured the solubilities of the hydroxyquinolates and anthranilates of manganese(II), zinc, iron(II), cadmium, cobalt(II), nickel, lead, copper(II), and palladium(II) ions in aqueous solutions. They were then able to show that the *ratios* of the solubilities were functions of certain properties of the ions and of the lattice energies of the salts. The reasoning involved is as follows.

The isothermal, reversible work of dilution (the dilution of a solution of a given initial concentration to the saturation concentration) is first calculated for a salt MX_2. Complete dissociation of the salts (all of the same type) is assumed, according to:

$$MX_2 \rightarrow M^{++} + 2\,X^- \tag{1}$$

If we begin with one mole of M^{++} and two moles of X^-, both at unit activity, upon diluting to the saturation concentration $C_{M^{++}}$ and C_{X^-} of the salt MX_2, the osmotic work* obtained is:

$$A'_s = RT \ln (1/C_{M^{++}}) + 2RT \ln (1/C_{X^-}) = -RT \ln C^2_{X^-} C_{M^{++}} \tag{2}$$

$$= -RT \ln S_{MX_2} \tag{3}$$

Starting with one mole of metal M and two moles of *uncharged* X radical, we can next determine the free energy of formation of the solid salt. This is obtained in two steps: (*1*) ionization of M and 2 X in their molar solutions, which gives us the electrical energy $2F(E^0_{M^{++}} + E^0_{X^-})$, and (*2*) dilution of the ions to their saturation concentrations, as above. ($E^0_{M^{++}}$ and $E^0_{X^-}$ are the standard potentials of M and X, respectively.) The total free energy is:

$$A = 2F(E^0_{M^{++}} + E^0_{X^-}) - RT \ln S_{MX_2} \tag{4}$$

From M and 2 X, the heat of formation, U, of MX_2 may be obtained from the relation:

$$U = A + T\Sigma S \tag{5}$$

Combination of Equations (4) and (5) gives:

$$RT \ln S_{MX_2} = 2F(E^0_{M^{++}} + E^0_{X^-}) - U + T\Sigma S \tag{6}$$

in which the last term is the product of the absolute temperature and the entropy changes in the formation of MX_2.

* Throughout the following discussion the original terminology of Treadwell and Ammann has been used. Their free energy, A, is the Helmholtz free energy, comparable with the Lewis and Randall function, F.

For two salts with a common anion, having solubility product constants S_1 and S_2, Equation (6) becomes:

$$RT \ln (S_1/S_2) = 2F(E_1^0 - E_2^0) - (U_1 - U_2) + T(\Sigma S_1 - \Sigma S_2) \quad (7)$$

The various terms may be evaluated as follows:

(*a*) The difference in the standard potentials may be calculated from published data.[2]

(*b*) Differences in heats of formation may be estimated from the Born-Haber cycle. In this stepwise cyclic process the heat of formation of a crystal is obtained, first by direct combination of the uncharged lattice constituents, and then by vaporization of the crystal components, ionization of these in the vapor state, and combination of the gas ions to form the lattice. In the second part of the cycle, the initial step involves heats of vaporization, λ; the second step involves the ionization energy, I, of the metallic vapor and the electron affinity of the X radical; and the third step involves the lattice energy, E_L, of the salt. Again, since we are concerned with differences, the various constants for the X radical need not be known, and the difference in heats of formation becomes:

$$(U_1 - U_2) = -(\lambda_1 - \lambda_2) - F(I_1 - I_2) + (E_{L_1} - E_{L_2}) \quad (8)$$

For the low-melting metals, the heats of vaporization are known within a few per cent, but for the high-boiling metals the uncertainty in the heats of vaporization is much greater. No data are available for the heat of vaporization of maganese, but it is estimated as about 80 kg.-cal. (somewhat lower than iron) at room temperature. Other data are obtainable from tables given by Eucken.[3] The ionization potentials are obtainable from tables given by Kuhn,[4] and their accuracy is reasonably great.

No data are available on differences in lattice energies. However, certain assumptions can be made in connection with the evaluation of this term (see the following discussion).

(*c*) The difference in the entropy changes $(S_1 - S_2)$ is derived readily from:

[2] W. M. Latimer, *Oxidation Potentials*. Prentice-Hall, New York, 1938.
[3] A. Eucken, *Metallwirtschaft*, 15, 27 (1936).
[4] H. Kuhn, *Atomspektren*. Akadem. Verlagsgesellschaft, Leipzig, 1934.

$$\Sigma S_1 = 2\,S_X + S_{M_1} - S_{M_1X_2} \tag{9}$$

$$\Sigma S_2 = 2\,S_X + S_{M_2} - S_{M_2X_2} \tag{10}$$

$$\Sigma S_1 - \Sigma S_2 = (S_{M_1} - S_{M_2}) - (S_{M_1X_2} - S_{M_2X_2}) \tag{11}$$

Now, for simple *ionic* crystals, the entropy of the lattice is given empirically by:

$$S = \tfrac{3}{2}\,R \ln (\text{mol. wt.}) + K \tag{12}$$

The constant K is presumably the same for salts of similar type.

The values thus obtained for entropies cannot be anything but extremely rough, when we consider that Latimer's equation was never intended for crystals in which the binding is not predominately ionic. Fortunately, the contribution of this term in the final equation for the ratio of solubility products is small. Using Equation (12), we obtain:

$$-(S_{M_1X_2} - S_{M_2X_2}) = -\tfrac{3}{2}\,R \ln (M_1/M_2) \tag{13}$$

in which M_1 and M_2 are the atomic weights of the cations whose solubility products are being compared. Data for entropies of the metals are given by Kelley.[5]

Now, substituting in (7), we obtain:

$$RT \ln (S_1/S_2) = 2F(E_1^0 - E_2^0) + (\lambda_1 - \lambda_2) + F(I_1 - I_2) - (E_{L_1} - E_{L_2}) + T(S_{M_1} - S_{M_2}) - \tfrac{3}{2}\,RT \ln (M_1/M_2) \tag{14}$$

Combining the terms for which evaluations can be made and designating these as Σ_i, Equation (14) becomes:

$$RT \ln (S_1/S_2) = \Sigma_i - (E_{L_1} - E_{L_2}) \tag{15}$$

Some general conclusions may be drawn from Equation (15). For isomorphous salts with the same anion, the difference in lattice energies would be zero, and solubility differences would depend entirely on Σ_i. For this conclusion, the cation diameters are assumed to be equal; however, when, in spite of equal cation diameters, there are still appreciable differences between RT ln (S_1/S_2) and Σ_i, these discrepancies may be accounted for on the basis of the differences in polarizability of the two lattice types.

When Σ_i is small, and yet the ratio of solubility products is large, a decided difference in lattice energies must exist. This would be the result of either (*a*) unequal ionic radii of the cations, and(or) (*b*) differences in polarizability of the lattices.

[5] K. K. Kelley, *U. S. Bur. of Mines, Bull.*, **350** (1932).

This approach to the solubility problem has been applied by Treadwell and Ammann to a study of the relative solubilities of alkali chlorates, perchlorates, and permanganates, and to the relative solubilities of some organometallic compounds of the type used in quantitative analysis. They measured the solubilities of some anthranilates and hydroxyquinolates of divalent metals in 1 *N* acetic acid, starting in each case with the pure salt. The solubility product, given by:

$$S = (M^{++})(X^{-})^2 = (M^{++})K_{ion}^2(HX)^2/(H^+)^2 \qquad (16)$$

becomes, in this case where $2(M^{++}) = (HX)$:

$$S = 4(M^{++})^3K^2/(H^+)^2 \qquad (17)$$

Then, for two salts which have a common anion and whose solubilities are measured in the same acid:

$$S_1/S_2 = (M_1^{++})^3/(M_2^{++})^3 \qquad (18)$$

In Table VIII are given their data on the solubilities and solubility product constants of the anthranilates and hydroxyquinolates; and in Table IX are given the invariant sums, Σ_i, for the divalent metals, ar-

TABLE VIII

Solubilities of Anthranilates and Hydroxyquinolates

Salt	Anthranilate			Hydroxyquinolate		
	Solubility in 1 *N* acetic acid, mole/liter	$4(M^{++})^3$	$RT \ln (S_1/S_2)$	Solubility in 1 *N* acetic acid, mole/liter	$4(M^{++})^3$	$RT \ln (S_1/S_2)$
Mn	1.82×10^{-2}	2.41×10^{-5}		1.45×10^{-2}	1.25×10^{-5}	
			1.73			2.02
Zn	6.92×10^{-3}	1.33×10^{-6}		4.09×10^{-3}	2.74×10^{-7}	
			−1.15			−2.04
Fe	1.24×10^{-2}	7.63×10^{-6}		5.90×10^{-3}	8.35×10^{-7}	
			−0.23			−1.07
Cd	1.41×10^{-2}	1.12×10^{-5}		1.08×10^{-2}	5.04×10^{-6}	
			2.22			2.65
Co	4.12×10^{-3}	2.80×10^{-7}		2.45×10^{-3}	5.88×10^{-8}	
			0.95			0.19
Ni	2.43×10^{-3}	5.74×10^{-8}		2.20×10^{-3}	4.26×10^{-8}	
			−3.33			−5.08
Pb	1.56×10^{-2}	1.52×10^{-5}		3.67×10^{-2}	2.13×10^{-4}	
			5.00			7.50
Cu	9.03×10^{-4}	2.95×10^{-9}		5.70×10^{-4}	7.41×10^{-10}	
			3.72			4.25
Pd	1.13×10^{-4}	5.77×10^{-12}		5.20×10^{-5}	5.73×10^{-13}	

TABLE IX

Values for Some Divalent Metals

	Mn-Zn	Zn-Fe	Fe-Cd	Cd-Co	Co-Ni	Ni-Pb	Pb-Cu	Cu-Pd
$2F(E_1^0 - E_2^0)$	15.7	15.0	1.4	3.7	4.6	4.6	21.2	22.2
$F(I_1 - I_2)$	−95.5	67.1	−32.7	17.3	−14.5	87.5	−125.6	5.1
$\Sigma_1 - \Sigma_2$	32.2	−54.4	58.0	−55.6	−3.0	36.0	−25.0	−10.6
$T(S_{M_1} - S_{M_2})$	−0.8	1.0	−1.7	1.7	−0.1	−2.5	2.3	−0.3
$-\frac{3}{2} RT \ln (M_1/M_2)$	0.2	−0.1	0.6	−0.6	0.0	−1.1	−1.1	0.5
Σ_i	−48.2	28.6	25.6	−33.5	−13.0	127.5	−128.2	6.7
Σ_i (corrected)	−18.2	0.0	55.6	−63.5	−13.0	154.5	−128.2	6.7
Ionic radius, Å.	Mn 0.91	Zn 0.83	Fe 0.83	Cd 1.03	Co 0.82	Ni 0.78	Pb 1.32	Cu 0.77 Pd 0.78
Difference in ionic radius, Å.	+0.08	0.0	−0.20	+0.21	+0.04	−0.54	0.55	−0.01

TABLE X

Calculated Ratios of Solubilities of Some Sulfides

	Mn-Zn	Zn-Fe	Fe-Cd	Cd-Co	Co-Ni	Ni-Pb	Pb-Cu	Cu-Pd
Difference in ionic radius, Å.	0.08	0.0	−0.2	0.21	0.04	−0.54	0.55	−0.01
Σ_i (corrected)	−18.2	−1.4	55.6	−63.5	−13.0	154.5	−128.2	6.7
$-(E_{L_1} - E_{L_2})$[a]	22.2	0.0	−51.9	55.5	11.1	−130	132.0	−1.9
$RT \ln (S_1/S_2)$	4.0	−1.4	3.7	−8.0	−1.9	24.5 (?)	3.8	2.8

[a] Calculated according to Equation (19), with $K = 1850$ and $r_A = 1.74$ Å.

TABLE XI

Calculated Ratios of Solubilities of Anthranilates and Hydroxyquinolates

	Mn-Zn	Zn-Fe	Fe-Cd	Cd-Co	Co-Ni	Ni-Pb	Pb-Cu	Cu-Cd
Difference in ionic radius, Å.	+0.08	0.0	−0.2	0.21	0.04	−0.54	0.55	−0.01
Σ_i (corrected)	−18.2	−1.4	55.6	−63.5	−13	154.5	−128.2	6.7
$-(E_{L_1} - E_{L_2})$[1]	27.6	0.0	−63.5	68.0	15.6	−156.5	160.0	−3.9
$RT \ln (S_1/S_2)$	9.4	−1.4	−7.9	4.5	2.6	−2.0	31.8(?)	2.8
$RT \ln (S_1/S_2)$ for anthranilates (exptl.)	1.73	−1.15	−0.23	2.22	0.95	−3.33	5.00	3.72
$RT \ln (S_1/S_2)$ for hydroxyquinolates (exptl.)	2.02	−2.04	−1.07	2.65	0.19	−5.08	7.50	4.25

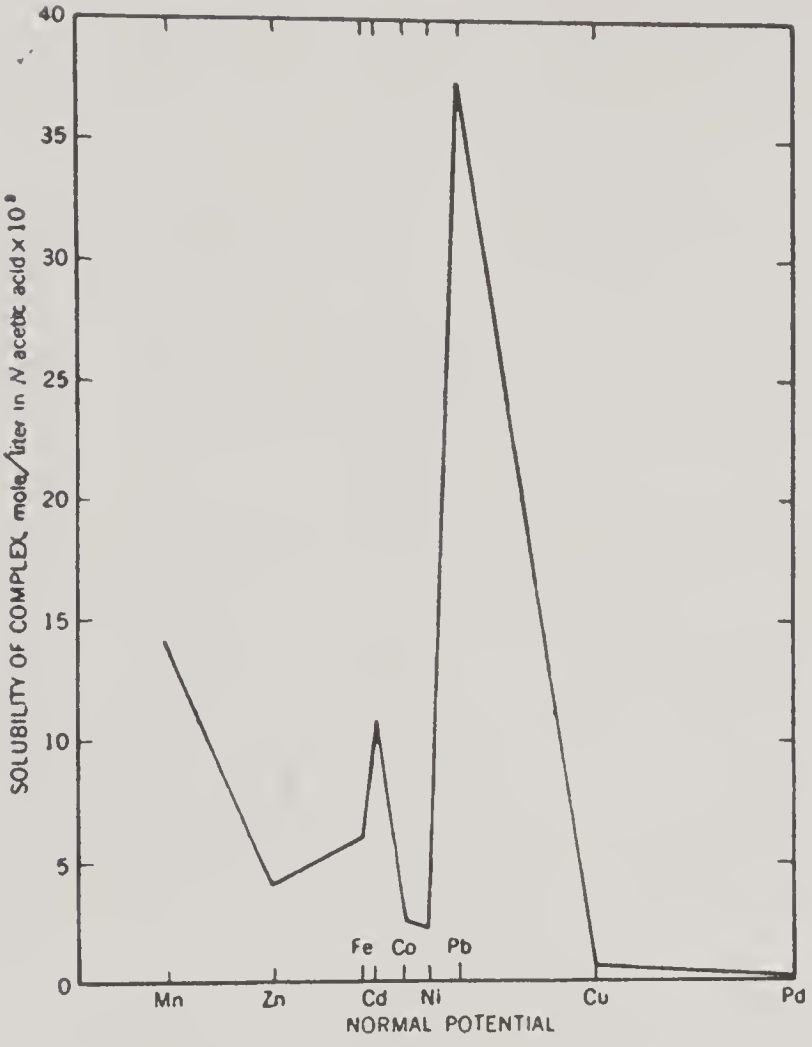


Fig. 5. Solubility of oxyquinolates.

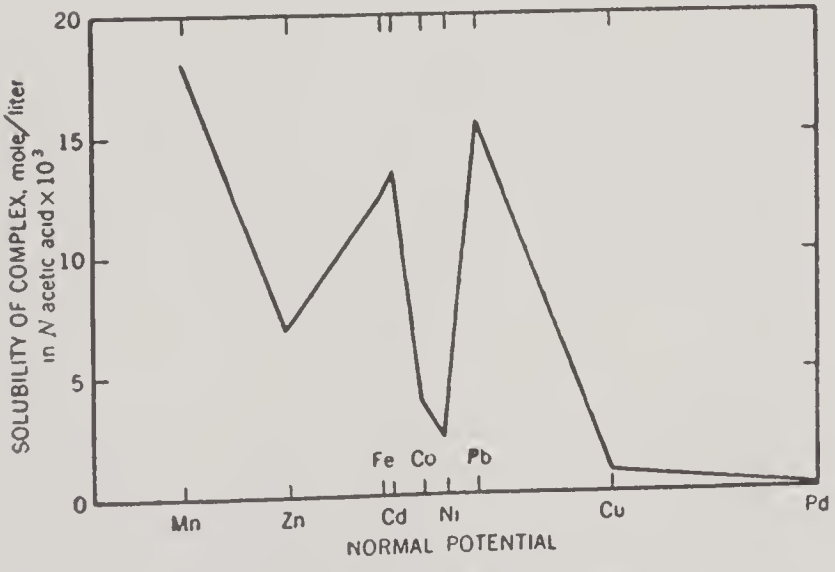


Fig. 6. Solubility of anthranilates.

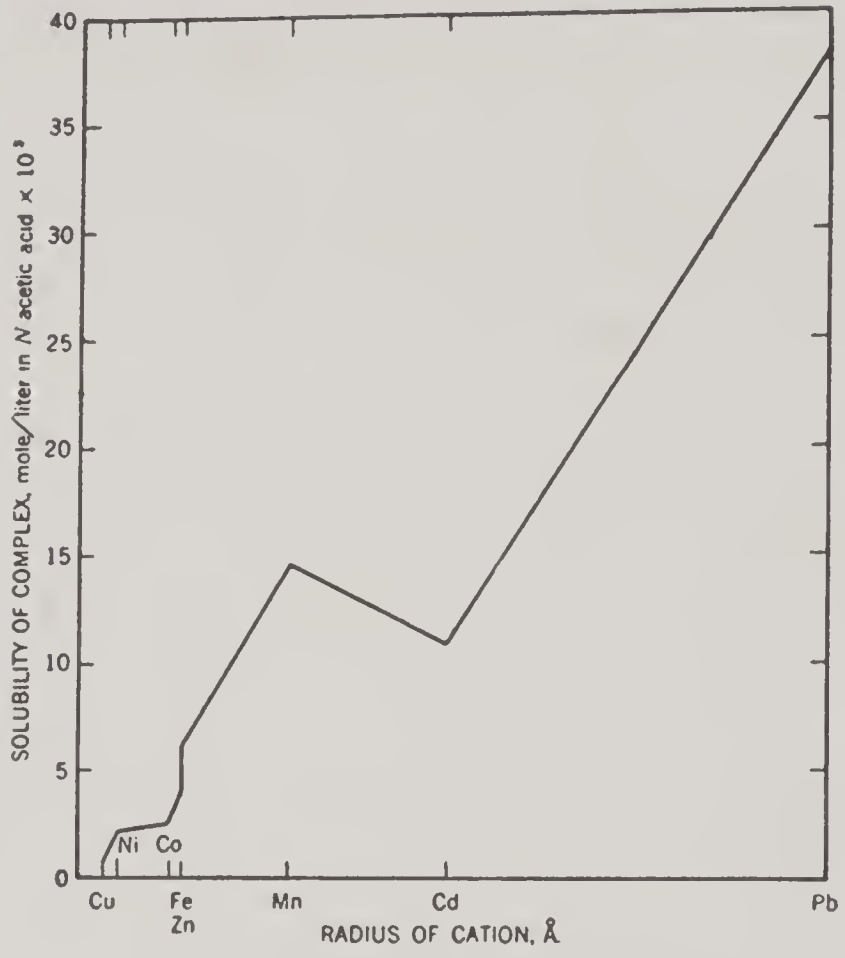


Fig. 7. Solubility of oxyquinolates.

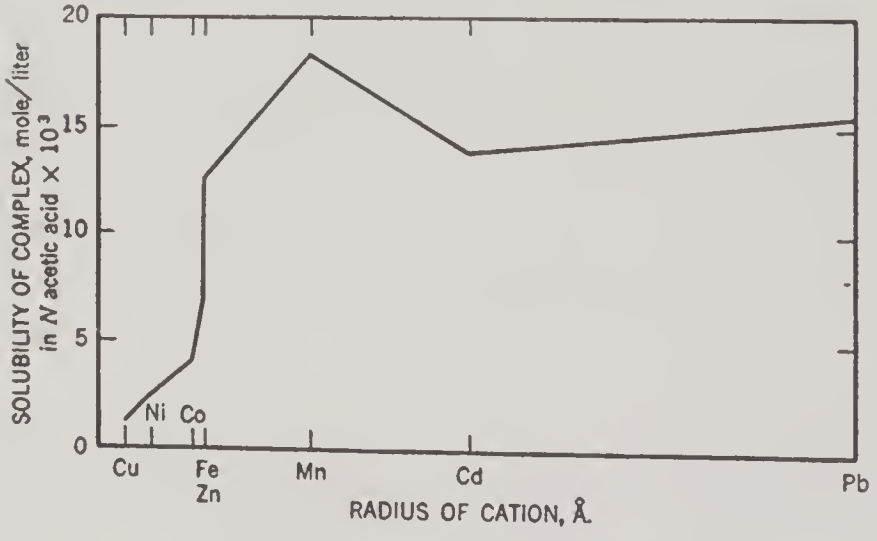


Fig. 8. Solubility of anthranilates.

ranged in order of increasing positive normal potential. The ionic radii, together with their differences, are presented in the last two rows. The radii of Cu^{++} and Pd^{++} are taken as 0.77 Å. and 0.81 Å., re-

spectively. The differences in lattice energies of the anthranilates and hydroxyquinolates, calculated from Equation (15), are given in Table X.

The striking similarities in the solubilities of the anthranilates and hydroxyquinolates are shown in Figures 5 to 8. In Figures 5 and 6 the solubility of the complexes (in moles per liter) is plotted against the standard potential of the cation, and in Figures 7 and 8 it is plotted against the radius of the cation.

From the data presented in Table IX, it will be seen that the ions, Zn and Fe, are of equal ionic radii. In this case, the high value of 28.6 kg.-cal. for Σ_i is probably incorrect, for the difference in lattice energies should be very small, and, therefore, a small value for Σ_i would be expected. This is actually observed in the case of the sulfides of zinc and iron; the solubility of zinc sulfide is 7.06×10^{-5}, of zinc blende, 6.63×10^{-6}, and of ferrous sulfide, 7.01×10^{-5}. For the sulfides, then $RT \ln (S_{ZnS}/S_{FeS})$ is at most -1.4 kg.-cal., which makes it appear that the calculated value in Table IX is about 30 kg.-cal. too high. This discrepancy is assumed to be due to the energy difference between normal iron vapor and that from which the ionization energy was calculated. This would account for the 30 kg.-cal. as energy of dissociation of the polymerized vapor, and as energy of activation of the dissociated products. Similar energy differences are to be expected in the case of other metals similar to iron and in the case of manganese. Thus, a correction of 30 kg.-cal. is applied to appropriate values in Table IX, giving the Σ_i (corrected) values.

The differences in lattice energy for the various anthranilates and hydroxyquinolates are presented in Table XI. It is assumed that the lattice energy of the complex is determined primarily by the distance of the cation from the point of combination in the anion. If this distance is r_A, and the radii of two cations are r_{c_1} and r_{c_2}, then:

$$E_{L_1} - E_{L_2} = K\frac{1}{r_A + r_{c_1}} - \frac{1}{r_A + r_{c_2}} \tag{19}$$

in which K is an empirical factor.

In the case of the organometallic complexes, r_A would be equal to half the C—O distance, or about 0.76 Å. Now, the differences in lattice energy may be calculated by Equation (19), with a value of $K = 920$ (which was presumably fitted to the data). From the calculated difference in lattice energies $(E_{L_1} - E_{L_2})$, the ratio of solubility products is computed and compared with the value obtained experi-

mentally. The ratios are of the same sign and order of magnitude—fairly good agreement, if one considers the number and kind of assumptions made. Similar success was found by the authors in predicting the ratios of the solubilities of some sulfides.

It is noted that the distance between the cation and the place of binding in the anion, *i.e.*, r_A, is of greatest importance in determining the solubility of these complex salts. A change of a few hundredths of an Ångstrom unit can change the difference in lattice energy by several kilogram-calories and thus affect the agreement between observed and calculated solubility ratios.

It is, therefore, understandable why anions, which react with metals forming five- or six-membered rings, react preferentially with those having a radius of about 0.76 Å. Under these conditions, the least strain is placed on the anion. The large ions (*e.g.*, lead) or the alkaline earths (strontium or barium) are best suited for the closing of four-membered rings containing an oxygen and nitrogen atom, or two oxygen atoms.

From the point of view of analytical chemistry, the primary value of investigations of this sort probably lies in the fact that these studies point the way to new experiments, and to the type of information needed for an accurate picture of the solubilities of organometallic complexes. This is a quantitative approach to the problem of solubility. Such studies may also be useful in predicting the relative solubility of the anthranilate or hydroxyquinolate of an ion not specifically mentioned or determined beforehand. It will be noted that the nature of the anion is not considered anywhere except in the calculation of r_A. Thus, a similar series of values of solubilities would exist for salts of other precipitants.

The last point mentioned is, in a sense, a weakness in this sort of theoretical approach to the solubility problem. It gives no additional indications about the type of molecule required to produce an organometallic complex of a desired degree of insolubility. Indeed, this theory depends in application on the existence of numerous insoluble salts of a given reagent; this also limits its usefulness. Other obvious weaknesses are: (*1*) the use of Latimer's equation for the entropy of the crystals, (*2*) lack of good data on heats of vaporization for iron, manganese, etc., and (*3*) introduction of the parameter K in evaluating differences in lattice energies, and the method of evaluation of K.

This work is presented because of its general interest and its bearing

on the fundamental physical chemistry of the organometallic compounds, rather than because of any immediate practical value.

Summary

The ratios of the solubilities of a series of salts with a common anion can be expressed in terms of the standard potentials of the metals, their ionization potentials, heats of vaporization, and entropies, as well as the entropy of the salt crystal and the lattice energies. For a series of salts with a common anion, the differences in lattice energy are frequently responsible for differences in solubility; or, if the salts are isomorphous, the other quantities determine the relative solubilities. If assumptions with regard to the lattice energies are made, a fair prediction of relative solubility is possible.

CHAPTER V

Techniques in Gravimetric and Volumetric Analysis with Organic Reagents

This chapter will be concerned with those special points of procedure and technique which are more or less unique in the use of organic reagents in gravimetric and volumetric analysis. The object will be to provide working directions, of a somewhat general nature, that will facilitate the performance of analyses with organic reagents.

A. Preparation and Purification of Organic Reagents

1. Preparation

The analyst is rarely concerned with this branch of the subject. All the common reagents, as well as many of the less familiar ones, are obtainable from commercial sources. If a given reagent must be synthesized for any purpose, the original literature pertaining to the use of that reagent should be consulted and syntheses by reliable methods are usually reported. Among other sources of information are the Beilstein *Handbuch* and the *Organic Syntheses* series; the latter contains procedures for preparing such common reagents as benzoin (oxime), cupferron, α-nitroso-β-naphthol, dimethylglyoxime, arsanilic acid, phenylarsonic acid, aluminon, and isatin (oxime).

2. Purification

The state of purity of an organic reagent, whatever its source, is of great importance. The principal impurities may be classified as organic and inorganic, and a brief consideration of these may prove worthwhile.

Organic Impurities. These are generally in the nature of by-products of the synthesis, and their presence or absence will depend almost entirely on the procedures employed in making the reagent. Hence, no general statements concerning them can be made, although the following points should be considered.

(*a*) If the impurities combine with the substance being precipitated, an incorrect weight of precipitate will be obtained. In many cases this may not prove serious, especially if: (*1*) the molecular weights of precipitant and impurity are not substantially different. (*2*) the percentage of impurity is small, and (*3*) the percentage of metal in the precipitate is small.

In the event that the precipitate is to be dissolved and analyzed volumetrically, *e.g.*, by the bromination technique (see page 87), an error may also be introduced. This will be the case if the impurity can be brominated to a greater or lesser extent than the precipitant itself; otherwise, its presence would make no difference.

(*b*) If the impurities do not combine with the substance being precipitated, they may cause no harm provided that they are: (*1*) completely soluble under the conditions of precipitation, (*2*) they do not decompose to give insoluble products under these conditions, and (*3*) they do not inhibit the principal reaction through complex formation or other means. Generally, the method of synthesis will indicate the probable nature of the impurities.

Whenever an organic reagent is used in a standard solution, as in an amperometric titration, it is well to standardize with the metal being determined, although satisfactory results were obtained when such solutions are prepared by direct weight (see pages 128 and 153).

Inorganic Impurities. Likewise, inorganic impurities may be introduced in the preparation, but they are more limited as to variety. Metallic ions, such as tin, may be present following the use of stannous chloride in some reduction process, or chloride ion may be found after the formation of an oxime with hydroxylamine hydrochloride. In the majority of cases these are trace impurities, and the nature of the substance being precipitated determines whether the impurity is harmful. Particular care should be exercised in interpreting the qualitative reactions of organic reagents, for the observed reaction may result from an impurity.

By way of general precaution, melting points should be taken for any organic reagent used if possible (some reagents such as cinchonine, cupferron, the arsonic acids, etc., decompose without melting). Likewise, the reagent may be recrystallized if its purity is suspected. Alcohol, benzene, and glacial acetic acid are the solvents commonly used; occasionally petroleum ether proves very useful, as in the recrystallization of salicylaldoxime. Following recrystallization, the re-

agent may be dried for a short time (30 minutes) at 50–60°C. The practice of the analytical chemist of drying all solids at 105–110°C. for an hour or so may lead to disaster in the case of many organic compounds which decompose readily at that temperature. For all highly critical work, and especially for trace analyses, the purification of organic reagents is strongly recommended. It is always essential if the melting point indicates contamination of the reagent.

Specifications for a few organic reagents have been drawn up by the Committee on Analytical Reagents of the American Chemical Society. Their reports cover at the present writing only dimethylglyoxime and 8-hydroxyquinoline. It is to be hoped that other reagents will be added to the list in the near future. Details of the specifications are given in the appropriate chapters (see pages 145 and 163).

B. Solutions of Organic Reagents

With the exception of the organic solvents, which are used in pure form, the organic reagents used in quantitative analysis must be made up in solution. Accordingly, a number of factors should be considered in this connection. These include solvents, concentration of reagents, and stability of the solutions.

1. Solvents

(*a*) *Water* is a satisfactory solvent for many organic reagents, including anthranilic acid, quinaldic acid, tannic acid, the sodium salt of dimethylglyoxime, uranyl zinc acetate, cupferron, and others. Wherever possible such aqueous solutions should be used: the danger of possible coprecipitation of the reagent is eliminated, as are possible solvent effects on the organometallic precipitate.

(*b*) *Organic solvents*, such as alcohol or acetic acid, are used for dissolving reagents which are more or less insoluble in water, *e.g.*, α-benzoin oxime, dimethylglyoxime. The solvent chosen should be miscible with water.

(*c*) *Combined solvents*, like water–alcohol, or water–acetic acid, are used for organic reagents which are only moderately soluble in water, but soluble in alcohol or acetic acid. The reagent may first be dissolved in a small amount of organic solvent, and then diluted with water to the proper concentration. Solutions of salicylaldoxime (alcohol), 8-hydroxyquinoline (glacial acetic acid), and α-nitroso-β-naphthol, among others, are prepared in this manner.

In one instance, at least, the reagent has been synthesized directly in the solution in which it is used. Thus, salicylaldehyde in alcohol and hydroxylamine hydrochloride in water are combined directly to give a solution of salicylaldoxime which may be diluted to the required strength.

In quantitative work, precipitation of the reagent itself, or of impurities in it, must always be considered, since it is particularly apt to happen when an excess of a water-insoluble reagent is used in a precipitation. If the precipitate is to be ignited, no harm is done; otherwise, positive errors will result. The difficulty may be avoided by the following procedures: (*1*) Precipitation from a solution containing a large amount of organic solvent. For example, in the precipitation of copper with 5,7-dibromo-8-hydroxyquinoline, the acetone solution of the reagent is added to the solution containing copper which has been made up to 50% acetone by volume. This practice is expensive and undesirable because of the possible solvent effect of the organic solvent on the organometallic complex. Small amounts of alcohol are sometimes used to prevent the precipitation of 8-hydroxyquinoline, although again the solvent action of the alcohol on the metallic complexes may be a disadvantage. (*2*) Precipitation from hot solution—a procedure sometimes used in combination with procedure *1*. (*3*) Use, where possible, of the sodium salts of reagents rather than the reagent itself. Therefore, while dimethylglyoxime is insoluble in water, its sodium salt is extremely soluble. Sodium anthranilate and sodium quinaldate are also used in preference to the free acids.

In certain cases, the *p*H of the solution may influence the solubility of the reagent in another way. Some reagents, *e.g.*, 8-hydroxyquinoline, precipitate at a moderately high *p*H from solutions in which they are soluble at a lower *p*H, and may then redissolve at a still higher *p*H.

2. Concentration of Reagents

The theoretical factors of importance in considering the concentration of the reagents are discussed in Chapter III. In practice, concentrations are usually expressed as per cent by weight, and one or two per cent solutions are most frequently used. The solubility of the reagent itself is about the only limitation on the strength of a solution, although too dilute a reagent will increase volumes unnecessarily, and too concentrated a reagent may cause over-rapid precipitation, espe-

cially locally, and lead to nonequilibrium conditions. Optimum concentrations for the various reagents are given in the chapters describing their uses.

3. Stability

The stability of solutions of organic reagents depends almost entirely on the nature of the reagent, rather than on the solvent. Aside from this no general rules can be formulated. The principal types of decomposition encountered seem to be photochemical and hydrolytic. Reagents like anthranilic acid and salicylaldoxime are subject to photochemical decomposition, and reagents like cupferron and salicylaldoxime decompose slowly by hydrolysis. Brown bottles are recommended as containers for the reagents which are likely to decompose photochemically, and for all reagents as a precautionary measure. Naturally, if the reagent decomposes readily, fresh solutions should be prepared at frequent intervals.

The *p*H of the reagent solution is doubtless a factor in determining its stability. For example, solutions of acid reagents appear less stable in alkaline than in neutral or weakly acidic solutions (anthranilic acid). Oxime reagents tend to hydrolyze in acidic solutions, and therefore neutral or weakly acidic conditions are required.

In general, the known conditions for maximum stability of a reagent is given under the discussion of that reagent in later sections.

C. Conditions for Precipitation

The conditions for precipitation with organic reagents differ little from the conditions followed generally in gravimetric analysis. Some factors which must be considered as unique for organic reagents are discussed in the following pages:

1. pH Control

The theoretical aspects of *p*H in precipitations with organic reagents have been presented in Chapter III. Once the proper *p*H for a precipitation has been decided upon, adjustment is made by adding acid or base to the solution (before adding precipitant), by means of some electrometric device for measuring *p*H, generally a glass electrode, or by means of indicator papers, particularly the "universal" type. The glass electrode obviously permits close adjustment of *p*H, and is most useful when separations are to be made (see page 60). Factors limit-

ing its use are: (*a*) the ordinary variety can be employed only at temperatures up to 40°C., which means that for precipitations which are to be made at the boiling point, *p*H must often be adjusted in the cold; (*b*) in solutions containing appreciable quantities of organic solvents, such as acetone or alcohol, the glass electrode may give erroneous values or be slow in reaching equilibrium. The indicator papers (Nitrazine, Hydrion, etc.), on the other hand, are convenient but not highly accurate. In many cases, however, their accuracy is sufficient, especially when a single substance is being precipitated, or when the "safe range" of *p*H in a separation is wide.

It should be recalled that the precipitant itself will cause a change in the *p*H of the solution. This effect is manifest in cases in which the precipitant is a fairly strong acid or base, and the solution is poorly buffered. The H^+ liberated in the reaction:

$$M^{++} + 2\,HX \rightleftharpoons 2\,H^+ + MX_2 \qquad (1)$$

may even in some cases be titrated as a means of determining the metal. Also, since some reagents, *e.g.*, 8-hydroxyquinoline, are used in acetic acid solution, the effect of this acid on the net *p*H of the solution must be considered. In such instances, preliminary adjustment of the *p*H to a value slightly *higher* than that finally desired may be a useful procedure.

In general, it is inadvisable to adjust the *p*H after precipitation, although an increase in *p*H is more effective than a decrease (in bringing about greater precipitation). Redissolving the precipitated material is slow and uncertain, and, even though the correct *p*H may have been reached (*e.g.*, by acidifying after precipitation), equilibrium is attained so slowly that the results are completely unreliable.

2. Temperature of Precipitation

Very little is known concerning the temperature coefficient of solubility of the organometallic complexes. In view of their low solubility at room temperature, major solubility losses would not be expected to occur at elevated temperatures. Thus, precipitation from hot solution would have the same advantages (and disadvantages) as it does in the case of inorganic precipitations. Apparently in some instances (for example with quinaldate precipitates), the degree of hydration of the complex depends on the temperature of precipitation (and digestion). Obviously, the undesirable feature of hot precipitations, in cases in

which the precipitant is dissolved in alcohol or acetone, is that precipitation of the reagent itself will be favored as the solvent evaporates.

3. Rate of Precipitation

As in ordinary gravimetric analyses, the precipitation should be made as slowly and uniformly as possible. For this purpose, a dilute reagent solution, usually made up to one or two per cent by weight, should be added slowly. Stirring during the addition of the reagent is highly desirable, especially in making separations, when local concentration effects are to be avoided.

Since most organometallic precipitates are voluminous, the amount of ion actually precipitated should be kept small, in order to avoid slow filtration. In general, one hundred milligrams of an ion is sufficient for a single precipitation. With the precipitate in such a case weighing perhaps several hundred milligrams, the determination can be made with sufficient accuracy.

4. Digestion

The function of digestion in the case of organometallic precipitates is primarily flocculation or improvement of crystalline form and, in some cases, hydration. There is little evidence which indicates exactly what happens during the digestion period; the precipitates seem to adsorb electrolytes to only a very slight extent, so that the presence of adsorbed impurities seems unlikely. Coprecipitated substances might partially be removed during the digestion.

During the digestion some precipitates, particularly the hydroxyquinolates, tend to adhere to the walls of the beaker. This is avoided and subsequent transfer of the precipitate is made easier by the addition of a small amount of sodium taurocholate.

D. Filtration and Washing

With a moderate amount of organometallic precipitate, these operations present no unusual difficulties. The precipitates are collected on filtering crucibles after the supernatant liquid has been decanted in the usual manner. Either sintered glass or porous porcelain crucibles are suitable; the latter type are, of course, essential if the sample is to be ignited. Filters of medium to fine porosity are generally required. The crucibles may be cleaned by being placed in sulfuric acid–

dichromate cleaning solution for several hours or longer. Warm, dilute hydrochloric acid is also a good solvent for many precipitates.

The precipitates should be washed, either hot or cold, with a solution of about the same *p*H as the precipitation solution. Sometimes the wash liquid contains a small amount of precipitant (anthranilates, sodium uranyl zinc acetate). No general directions can be given. The use of organic wash liquids, such as alcohol, acetone, and ether, offers definite advantages in that the precipitates dry faster and collect more evenly in the crucible. However, specific solubility effects should be considered, and an organic wash liquid should be employed only when called for explicitly in the directions.

It has been reported[1] that strongly ammoniacal solutions, *e.g.*, the solution from which nickel dimethylglyoxime precipitates, have a solvent effect on sintered glass crucibles. Presumably, this is significant only in the determination of small amounts, but this point seems worthy of further investigation.

The last portion of wash liquid should, of course, be tested for precipitant; a small amount of the ion being determined is added to a sample of the solution, and, if precipitation occurs, further washing is necessary.

E. Drying (Ignition) and Weighing

If the organometallic complex has a definite composition and is stable, the precipitate is dried at a temperature of about 105–130°C., depending on its nature and the final state of hydration expected. Some of the drying temperatures for the common precipitates, and the compound obtained at that temperature, are given in the Appendix, page 283. Prolonged drying is undesirable only at higher temperatures, about 130–150°C., at which gradual decomposition may set in. Drying in a stream of air at room temperature is sometimes employed (see page 220).

If for any reason the complex cannot be dried to constant composition, it must be ignited. This is necessary in many instances, especially with α-nitroso-β-naphthol, tannin, and the arsonic acid and cupferron precipitates. Likewise, some hydroxyquinolates and salicylaldoximates must be ignited. Cupferron, α-nitroso-β-naphthol, tannin, and arsonic acid precipitates are ignited directly in filter paper; the oxine and salicylaldoxime precipitates are mixed with either oxalic

[1] V. Aleksandrov, *Zavodskaya Lab.*, **10**, 447 (1941); *Chem. Abstracts*, 38, 4216 (1944).

acid or ammonium nitrate before ignition. Details are contained in the appropriate chapters. Ignition is always undesirable insofar as it reduces the weight of precipitate, and thus indirectly the precision of the determination.

No special precautions are called for in cooling and weighing organometallic precipitates. Generally, these precipitates are nonhygroscopic, and may be handled by the usual techniques.

F. Calculation of Results

A table of gravimetric factors for most of the common organometallic weighing forms is given in the Appendix, page 283.

G. Volumetric Determinations

In many cases it may be more rapid and accurate to conclude a determination volumetrically rather than gravimetrically. This applies particularly to small amounts of precipitate in the weighing of which comparatively large errors would occur. The volumetric conclusion of a determination may involve the determination of either the organic or the inorganic constituent of the complex. These will be considered in detail.

The determination of the organic component is based on the simple fact that if a precipitate is of definite, known composition, the amount of organic component in the precipitate may be obtained and used to calculate the amount of metallic substance. The organic component may be determined in several ways: (*1*) by quantitative bromination, (*2*) by quantitative wet oxidation, (*3*) by hydrolysis, followed by oxidation of an hydrolysis product, or (*4*) by combustion analysis.

(*1*) The bromination technique is applicable to molecules that are rapidly and quantitatively brominated to give definite products; examples among the organic reagents are 8-hydroxyquinoline, anthranilic acid, and salicylaldoxime. The brominating reagent consists of a standard solution of potassium bromate, used in conjunction with potassium bromide in an acidic solution. Direct titration of the dissolved organometallic complex is generally not feasible; therefore a measured, excess amount of the bromate–bromide solution is added, and the excess is determined iodometrically.

A number of precautions are required to obtain accurate results by this method: (*a*) The precipitate to be analyzed must be completely free of excess precipitant; otherwise, results will be high. (*b*) Loss of

material during the dissolving of the complex and transfer of the solution must be avoided. (*c*) Loss of bromine during the bromination, which will cause the results to be too high, must likewise be avoided.

If proper precautions are taken, however, the method is capable of great sensitivity. As an example, let us consider the volumetric determination of aluminum hydroxyquinolate. The reactions involved are:

$$Al^{+++} + 3\ C_9H_6NOH \rightarrow Al(C_9H_6NO)_3 + 3\ H^+ \quad (2)$$

$$Al(C_9H_6NO)_3 + 3\ HCl \rightarrow Al^{+++} + 3\ C_9H_6NOH + 3\ Cl^- \quad (3)$$

$$KBrO_3 + 5\ KBr + 6\ HCl \rightarrow 3\ Br_2 + 6\ KCl + 3\ H_2O \quad (4)$$

$$C_9H_6NOH + 2\ Br_2 \rightarrow C_9H_4Br_2NOH + 2\ HBr \quad (5)$$

From Equations (2) and (5) it is evident that one atom of aluminum is equivalent to 6 Br_2; thus, its equivalent weight in this process is Al/12, or 2.248 g. Hence, 0.1 ml. of 0.1 *N* potassium bromate would correspond to 0.02248 mg. of aluminum. The use of microburets increases the useful range of such methods.

Table XII gives some precipitates, among others, that may be analyzed by this method, and the corresponding equivalent weights.

TABLE XII

Equivalent Weights of Some Precipitates in Bromate Titration

Precipitate	Equivalent weight in bromate titration
Copper anthranilate	$\frac{Cu(C_7H_6NO_2)_2}{12}$
Zinc anthranilate	$\frac{Zn(C_7H_6NO_2)_2}{12}$
Copper benzoin oxime	$\frac{Cu(C_{14}H_{11}O_2N)}{6}$
Nickel dimethylglyoxime	$\frac{Ni(C_4H_7N_2O_2)_2}{24}$
Aluminum hydroxyquinolate	$\frac{Al(C_9H_6NO)_3}{12}$
Magnesium hydroxyquinolate	$\frac{Mg(C_9H_6NO)_2}{8}$
Zinc hydroxyquinolate	$\frac{Zn(C_9H_6NO)_2}{8}$
Copper salicylaldoxime	$\frac{Cu(C_7H_6NO_2)_2}{14}$

In practice, the brominations are carried out in the following manner. First, the precipitate is formed, digested, filtered, and washed as already described. The precipitate in the crucible is next treated with 5–10 ml. of concentrated hydrochloric acid. When the precipitate has dissolved, suction is applied and the solution is drawn into a clean flask. The crucible is washed thoroughly with warm dilute hydrochloric acid. The solution is then transferred to an iodine flask, made up to about 2–3 *N* in hydrochloric acid, and diluted to about 100 ml. To this solution the standard potassium bromate may be added dropwise from a buret until an excess is present, as indicated by the color of bromine in the solution. Potassium iodide is then added, and the iodine is determined with standard thiosulfate. In the author's opinion, a better procedure is to add from a pipet an amount of bromate–bromide solution which is estimated to be in excess of the requirement, then to stopper the iodine flask quickly, and allow the bromination to proceed; 5–10 minutes is usually sufficient. Potassium iodide solution is next added through the cup on the iodine flask, and the iodine (which is used to measure the excess bromate) is determined with standard thiosulfate. A device for performing these operations without danger of loss of bromine is shown in Figure 9 below.

The metal content of the precipitate is calculated from the equivalents of bromate used (equivalents added less the equivalents of thiosulfate required to back-titrate), multiplied by the proper equivalent weight (Table XII).

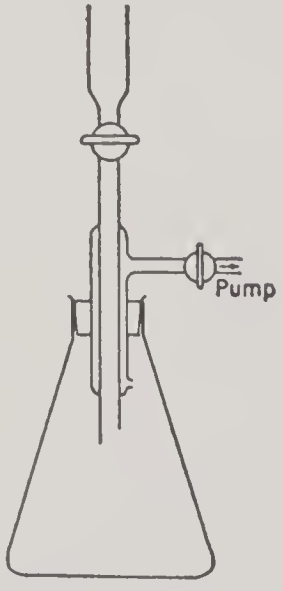


Fig. 9. Apparatus for quantitative brominations.

(*2*) The determination of the organic constituent of a precipitate by direct wet oxidation has been used in the case of magnesium hydroxyquinolate.[2] Perchloratoceric ion is employed to oxidize, in a reproducible but nonstoichiometric manner, the hydroxyquinoline portion of the magnesium hydroxyquinolate. An advantage of this particular procedure is the large number (29.5) of equivalents of oxidant consumed per mole of hydroxyquinoline.

[2] L. Gerber, R. I. Claassen, and C. S. Boruff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 658 (1942).

Alkaline permanganate will also oxidize a number of the common organic precipitants, although the difficulty in determining end points with this reagent tends to detract from its usefulness.

(*3*) A method for the determination of precipitates formed with oxime reagents should also be mentioned. These precipitates (which include copper α-benzoin oxime and nickel dimethylglyoxime) are dissolved in acid; the solution is then boiled to hydrolyze the oxime and the hydroxylamine thus formed is determined oxidimetrically. This may be done in either of two ways: (*a*) by oxidation with excess ferric sulfate, and titration of the ferrous iron formed with a standard oxidant, such as permanganate; or (*b*) by oxidation with excess standard bromate–bromide solution, and determination of the excess with arsenious acid.

These methods also have the advantage of sensitivity at low concentrations. For example, in the volumetric determination of nickel dimethylglyoxime, the following reactions are used:[3]

$$Ni^{++} + 2\,(CH_3)_2C_2(NOH)_2 \rightarrow (C_4H_6NONOH)_2Ni + 2\,H^+ \quad (6)$$

$$(C_4H_6N_2O_2H)_2Ni + 4HCl + 2H_2O \rightarrow Ni^{++} + 2\,Cl^- + 2\,NH_2OH{\cdot}HCl + 2\,C_4H_6O_2 \quad (7)$$

$$NH_2OH{\cdot}HCl + KBrO_3 \rightarrow HNO_3 + KBr + H_2O + HCl \quad (8)$$

$$2\,KBrO_3 + 3\,As_2O_3 + 10\,KBr + 12\,HCl \rightarrow 3\,As_2O_5 + 12\,KCl + 12\,HBr \quad (9)$$

In this case, four molecules of hydroxylamine, equivalent to one atom of nickel, are equivalent to four moles of bromate. Thus, the equivalent weight of nickel is 1/24 of the atomic weight, and 1 ml. of 0.1 *N* potassium bromate equals 0.2445 mg. of nickel.

A similar case is encountered with copper α-benzoin oxime, in which two moles of reagent, each containing one molecule of hydroxylamine, combine with one atom of copper, giving the copper an equivalent weight equal to 1/12 its atomic weight.

A case[3] might be mentioned in which simultaneous oxidation of hydroxylamine, and bromination of an aromatic nucleus occur. This is true of salicylaldoxime precipitates, which may be hydrolyzed to give hydroxylamine and salicylaldehyde. The latter substance is partially brominated and oxidized by the bromate–bromide mixture; the

[3] N. H. Furman and J. F. Flagg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 738 (1940).

hydroxylamine is also oxidized. Altogether, 14 equivalents of oxidizing agent are consumed per atom of copper.

(*4*) The microgasometric analysis of organometallic precipitates represents a somewhat unusual departure from the conventional methods employing organic reagents. The precipitated compound, weighing perhaps a few milligrams or less, is oxidized in the wet way by a mixture containing chromic and iodic acids. The carbon dioxide produced is then determined in a micromanometric apparatus. Since rather small amounts of carbon dioxide can be determined with accuracy by this method, it follows that micro quantities of organometallic precipitates can be readily determined. Details of methods for the determination of calcium as the picrolonate, and of sulfate as benzidine sulfate, by this technique are given on pages 224 and 238, respectively.

Finally, mention should be made of methods in which the precipitate is analyzed volumetrically by determining the inorganic constituent. One such method is the analysis of nickel dimethylglyoxime precipitates in which the nickel is determined by the conventional cyanometric titration.[4] Such methods do not appear to have been widely used, and indeed offer less by way of sensitivity than do methods based upon the determination of the organic portion of the precipitate.

H. Reclaiming Organic Reagents

If necessary, the organic reagent may be recovered from many types of organometallic complex. Obviously, this would only be profitable in cases in which large numbers of determination were made with a comparatively expensive or rare reagent.

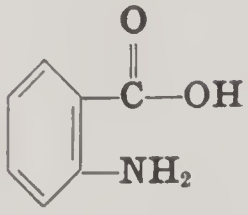
The reagent may be recovered by treating an aqueous suspension of the precipitate with hydrogen sulfide at the correct *p*H, or by transposing it with sodium hydroxide (see page 59). In both processes the solution, obtained after the precipitate has been filtered off, will contain the reagent, either as the acid or the sodium salt. Subsequent evaporation and recrystallization will yield a reagent suitable for reuse. Precipitants which are recoverable in this manner include 8-hydroxyquinoline, quinaldic acid, anthranilic acid, salicylaldoxime, and α-benzoin oxime.

[4] I. I. Pomerantz, *Zavodskaya Lab.*, **4**, 966 (1935); *Chem. Abstracts*, **30**, 985 (1936).

SPECIAL REAGENTS

CHAPTER VI

Anthranilic Acid



Molecular weight: 137
Melting point: 145°C.
Solubility: soluble in water, alcohol, acetone
Reagent solution: 1% solution of the acid in water, adjusted with sodium hydroxide to a *p*H of about 6

In weakly acid or neutral solutions anthranilic acid combines with ions such as cadmium, cobalt, copper, iron(II,III), lead, manganese(II), mercury(II), nickel, palladium(II), silver, and zinc to yield insoluble complex salts. Several of these salts, including the cadmium, cobalt, copper, and zinc compounds, are suitable for the quantitative precipitation and determination of these particular elements. The reagent itself is stable in water solution, is easy to obtain, and, in view of the considerable amount of work that has been done on the applications of anthranilic acid, it should find extensive use in analytical procedures.

Precipitations with anthranilic acid must be made a controlled *p*H, for, in too strongly acidic solutions, the organometallic precipitates will not form, while, in too strongly basic solutions, they are converted into either the metallic hydroxide or the corresponding ammonia complex, if the latter exists.

Goto[1] has given the limits of *p*H at the points of incipient and complete precipitation of various ions with anthranilic acid. Since concentrations of reactants are not indicated, these data cannot be regarded as valid for all solutions. The values are listed in Table XIII. It has also been noted[2] that Goto used acetate buffers in which the

[1] H. Goto, *J. Chem. Soc. Japan*, **55**, 1156 (1934).
[2] R. J. Shennan, J. H. F. Smith, and A. M. Ward, *Analyst*, **61**, 395 (1936).

TABLE XIII

*p*H for Precipitation of Anthranilates[a]

Element	pH for precipitation	
	Incipient	Complete
Cadmium	4.25	5.23
Cobalt	3.36	4.41
Copper	1.40	2.79
Manganese	4.10	5.15
Nickel	3.64	4.51
Zinc	3.76	4.72

[a] H. Goto, *J. Chem. Soc. Japan*, **55**, 1156 (1934).

cadmium, cobalt, nickel, and zinc anthranilates are soluble; hence, doubt is cast on the ultimate value of the data.

Although no separations appear to have been reported, the range of *p*H values suggests the possibility of making certain separations, *e.g.*, that of copper from cadmium or manganese.

TABLE XIV

Solubility Products of Anthranilates

Element	Solubility product
Cadmium	5.4×10^{-9}
Cobalt	2.1×10^{-10}
Copper	6.0×10^{-14}
Manganese	5.3×10^{-7}
Nickel	8.1×10^{-10}
Zinc	5.9×10^{-10}

The author has determined the solubility products of a number of insoluble anthranilates by the fractional precipitation method described on page 59; these are listed in Table XIV. In Table XV are given some calculated *p*H ranges for the separation of copper from cadmium, and copper from manganese. In practice these separations are none too satisfactory; apparently nonequilibrium conditions are set up, with the result that coprecipitation causes high values to be obtained for the element first precipitated, and correspondingly low values for the second element. There are more satisfactory reagents, such as salicylaldoxime, for the separation of copper from cadmium and manganese.

TABLE XV

Calculated *p*H Range for Precipitations by Anthranilic Acid

Element	Molarity of solution, $\times 10^3$	*p*H for precipitation	
		Incipient ($\alpha = 0$)	Complete ($\alpha = 0.99$)
Cadmium	2.5	4.1	—
Copper	4.8	—	2.9
Manganese	3.5	5.1	—

Thus, it is seen that a separation of the given amounts of copper and manganese should be possible through control of the *p*H. Actual tests, performed under the conditions stated in Table XVI, showed that within certain limits this was the case.

TABLE XVI

Separation of Copper from Manganese with Anthranilic Acid[a]

Copper taken, mg.	Manganese taken, mg.	Copper found, mg.	Manganese found, mg.
62.0	9.4	62.0	9.3
62.0	9.4	61.8	—
62.0	18.8	63.9	—

[a] *p*H = 2.9–4.1, anthranilic acid concentration = 0.02 *M*.

Thus, we see that anthranilic acid is limited in use to the precipitation of a single substance from a relatively pure solution, in which small amounts of alkali metals, alkaline earths, or ammonium salts may be present, or in which the concentration of heavy metal impurities is fairly accurately known; in the latter case, compensation may be made by control of the *p*H.

The presence of large quantities of ammonium, potassium, or sodium salts influences the completeness of precipitation of cadmium and zinc anthranilates (see Table XVII); similar effects might occur with other metallic anthranilates.

[3] H. Funk, *Z. anal. Chem.*, **123**, 241 (1942).

TABLE XVII

Effect of Foreign Salts on Precipitation with Anthranilic Acid[a]

Foreign salt, 3 g.	Zinc taken, mg.	Zinc found, mg.	Cadmium taken, mg.	Cadmium found, mg.
KNO_3	50	49.9	49.9	49.9
$NaNO_3$	50	49.9	49.9	49.8
NH_4NO_3	50	49.8	49.9	49.9
KCl	50	49.8	49.9	43.3
NaCl	50	48.4	49.9	43.2
NH_4Cl	50	48.7	49.9	36.0
K_2SO_4	50	49.3	49.9	49.6
Na_2SO_4[b]	50	49.1	49.9	49.4
$(NH_4)_2SO_4$	50	48.2	49.9	48.9
CH_3COOK	50	47.9	49.9	47.2
CH_3COONa[c]	50	47.3	49.9	46.2

[a] H. Funk, *Z. anal. Chem.*, **123**, 241 (1942).
[b] 7 g. $Na_2SO_4 \cdot 10\ H_2O$
[c] 5 g. $CH_3COONa \cdot 3\ H_2O$

As the *p*H is not given in any case, it is difficult to assess the results accurately. However, one might assume that the effect of ammonium chloride in dissolving cadmium anthranilate was due largely to the low *p*H such a salt would produce, although the effect of complex ion formation on the precipitation cannot be entirely ruled out. On the other hand, the acetates apparently have a specific effect, and *p*H alone is not the determining factor, since the *p*H of these solutions would be adequate for complete precipitation. The low degree of dissociation of numerous acetates has been recognized, and the solubility of the organometallic complexes in the presence of excess acetate may depend on this property. The entire subject is of utmost importance, and requires further investigation.

Anthranilic acid precipitates may be analyzed volumetrically by bromination with an excess of bromate–bromide mixture, followed by determination of the excess with thiosulfate. It has been reported[2] that the determination is most accurate when three bromine molecules are consumed per mole of anthranilic acid.

I. Determination of Cadmium[3]

The solution, which should contain 100 mg. or less of cadmium in a volume of 150 ml., should contain no free acid, no interfering elements, and no excessive amounts of neutral salts. Acid solutions should be evaporated to dryness, and the residue then taken up in the prescribed amount of water. After it has been made neutral to methyl

red with dilute sodium carbonate (3 g. $Na_2CO_3 \cdot 10\ H_2O$ per 100 ml. water), the solution is heated to boiling and precipitated with 25 ml. 3% sodium anthranilate. When the solution has cooled to room temperature, in about one hour, the precipitate is collected on a filtering crucible, washed first with 50–100 ml. of diluted (1:20) reagent solution and then with alcohol, and dried to constant weight at 105–110°C. The precipitate, $Cd(C_7H_6NO_2)_2$, contains 29.22% cadmium.

If desired, the determination may be concluded volumetrically. The washed precipitate of cadmium anthranilate is dissolved in 4–6 *N* hydrochloric acid, transferred to a flask, and titrated with standard potassium bromate (0.1 or 0.2 *N*) containing potassium bromide. The indicator used is a few drops of a solution, which is made up of 0.2 g. indigocarmine and 0.2 g. styphninic acid in 100 ml. water. The sample is titrated until the indicator changes from green to yellow, which indicates a slight excess of bromine. Several ml. of 0.2 *N* (4%) potassium iodide is added at once, the solution is diluted to an acid concentration of about 1.5 to 2 *N*, and the iodine is titrated with standard 0.1 *N* thiosulfate, with starch as the indicator. In this method, one molecule of anthranilic acid consumes two molecules of bromine, and the equivalent weight of cadmium is Cd/8, or 14.05.

The accuracy of the volumetric method may be increased[2] by a modified procedure. The cadmium anthranilate is precipitated, filtered, washed, and dissolved in hydrochloric acid, as described above. To the solution of the complex in an iodine flask is added sufficient standard bromate–bromide solution to brominate completely the two molecules of anthranilic acid and to leave an excess equivalent to 20–30 ml. 0.1 *N* thiosulfate; 1 ml. 0.1000 *N* bromate is equivalent to 0.9351 mg. cadmium. Bromination is complete in about 30 minutes. During this period, the iodine flask should be stoppered and the cup filled with 10 ml. 20% potassium iodide solution to prevent escape of bromine. The potassium iodide is finally allowed to run into the flask, and the iodine is titrated with standard thiosulfate; starch is added shortly before the end point is reached. As each molecule of anthranilic acid consumes three molecules of bromine, the equivalent weight of cadmium under these conditions is Cd/12 or 9.351.

A. Microdetermination of Cadmium

Accurate results are obtained if the prescribed techniques are carefully followed. Wenger and Masset[4] have made a thorough study

[4] P. Wenger and E. Masset, *Helv. Chim. Acta*, **23**, 34 (1940).

of this determination, and give detailed directions for optimum results.

With the microtechnique, from 1 to 7 mg. cadmium can be determined with an error of 0.3% or less. In the determination of 2-mg. samples of cadmium, it was found that no interference was caused by 10 mg. sodium acetate, 5 mg. sodium or potassium chloride, 100 mg. potassium nitrate, or 20 mg. potassium sulfate. A filter beaker or filter stick is recommended for small volumes of solution; the same general conditions of precipitation described for the macromethod should be used in the microdetermination. The precipitation should be made with a 0.2% solution of the reagent.

II. Determination of Zinc[2]

The sample to be analyzed should contain no more than 100 mg. zinc in 150 ml., and should be free from interfering elements and mineral acids. If nitric or hydrochloric acid is present, the solution is evaporated to a few drops; sulfuric acid solutions are taken to dryness; in both cases, evaporation is followed by dilution with water to about 150 ml.

If the removal of acid is not required, the solution is heated to boiling and treated with 20 ml. 3% sodium anthranilate. If acids are present, the solution is first made neutral to methyl red with dilute sodium carbonate (3 g. $Na_2CO_3 \cdot 10\ H_2O$ per 100 ml. water), and is then precipitated as described.

After the precipitate has stood for 10–15 minutes, it is collected on a filtering crucible of fine porosity, washed with cold, diluted (1:20) reagent and finally with alcohol, and dried to constant weight at 105–110°C. The precipitate, $Zn(C_7H_6NO_2)_2$, contains 19.36% zinc. If desired, the determination may be concluded volumetrically by either of the methods given on page 99. The equivalent weights of zinc are, respectively, 8.172 and 5.448.

A. Microdetermination of Zinc

The proper conditions for the microdetermination of zinc with anthranilic acid have been reported by Cimerman and Wenger.[5] A freshly prepared, 1% solution of anthranilic acid is added dropwise to 2–5 ml. of a solution containing not over 3 mg. of zinc at *p*H 6–7. Since the excess of about 0.3 ml., which is recommended, is said to be

[5] C. Cimerman and P. Wenger, *Mikrochemie*, 18, 53 (1935).

important, it is advisable to make a preliminary rough determination of the amount of zinc present in a sample. The mixture is stirred or shaken, allowed to stand for 15–30 minutes, and the precipitate is collected in a small filter tube or filter stick. The precipitate is washed first with 1–2 ml. of the 0.1% reagent solution, and then 5 or 6 times with 1–2 ml. portions of alcohol. The precipitate is dried for 15 minutes at 110–115°C., and weighed using proper microchemical technique.

The use of zinc anthranilate as a final weighing form for zinc, subsequent to the separation of that element from others by conventional methods, has been recommended in a number of cases. Details of two of the more useful methods are given.

B. Determination of Zinc in Tin–Lead Solder, and in White Metal Alloys[6]

This method is applicable to the determination of the semimicro-quantities of zinc present as an impurity in tin–lead solder in amounts ranging from 0.01 to 0.10%, and to the determination of the quantities of zinc which correspond to about the 8% found in zinc–tin alloys. The procedure may also be used for the determination of zinc in zinc chloride–ammonium chloride fluxes, and for the determination of zinc oxide in certain types of enamel.

1. Analysis of Solder and Zinc–Tin Alloys

The sample (0.5 g. solder or 0.05 g. zinc–tin alloy) is dissolved in concentrated hydrochloric acid which is saturated with bromine. When the sample has dissolved, 2 to 3 ml. concentrated sulfuric acid is added, and the solution is evaporated until fumes appear. After the solution has been carefully diluted, and the lead sulfate has been filtered off and washed with 2% sulfuric acid, 0.3 g. sodium tartrate is dissolved in the combined filtrate and washings to prevent the precipitation of tin. With litmus as the indicator, the *p*H of the solution is adjusted in three steps: (*1*) addition of saturated sodium hydroxide until the neutral point is almost reached, (*2*) addition of powdered sodium carbonate until the solution is just alkaline, and (*3*) addition of 2% acetic acid until the solution is neutral or slightly acidic. Then, 25 ml. of the sodium anthranilate reagent is added slowly with constant stirring. The solution is allowed to stand for at least 30 minutes

[6] C. W. Anderson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 367 (1941).

to insure complete precipitation of the zinc. Funk[3] reports that precipitation of zinc anthranilate from cold solutions leads to high results, and recommends that the complex be precipitated from boiling solution (see page 100).

The precipitate is collected on a filtering crucible, washed with diluted (1:15) anthranilic acid reagent, then finally with alcohol, and dried for 30 minutes at 100° to 105°C. The precipitate contains 19.36% zinc.

2. White Metal Alloys Containing Iron

A sample of 0.5 g. of the alloy is dissolved in concentrated hydrochloric acid saturated with bromine. When solution is complete, 1 g. potassium chloride is added, and the solution is evaporated to apparent dryness. The residue is broken up and heated at 100°C. until the odor of hydrochloric acid is very faint (5–7 min.). In the presence of potassium chloride it is possible to evaporate the solution to dryness without decomposition of ferric chloride. The residue is treated with 20 ml. water and heated (boiled if necessary) until a clear solution results.

A solution, containing 3 g. sodium acetate in 100 ml. water, is made neutral to litmus with 1% acetic acid; it is then added to the ferric chloride solution, and the mixture is diluted to 400 ml. and boiled for 1 minute. The basic acetate is filtered while hot, and the precipitate is washed with hot 1% ammonium acetate solution. The washing is continued until the volume is 600 ml. The filtrate is transferred to an 800-ml. beaker, 5 ml. concentrated sulfuric acid is added, and the solution is heated. Just before sulfur trioxide fumes appear, 5 ml. concentrated nitric acid is added to assist in the destruction of interfering ammonium salts. Evaporation is continued until dense fumes of sulfur trioxide appear. The solution is cooled, washed into a 150-ml. beaker, and evaporated to a volume of 15 ml. It is then made neutral to litmus, first by the addition of saturated sodium hydroxide, followed by the addition of powdered sodium carbonate until the reaction is alkaline; finally, the solution is made slightly acid with a few drops of 2% acetic acid. To the mixture is added 0.3 g. sodium tartrate, according to the regular procedure, and the zinc is precipitated by the addition of 25 ml. of the anthranilic acid reagent. Reprecipitation of the basic acetate does not seem to be required, as the original investigator found no entrainment of zinc with the iron precipitate.

3. Zinc Chloride Fluxes

Any convenient weight of sample is taken, dissolved in water containing a few drops of hydrochloric acid, and made up to some convenient volume. Aliquots are measured accurately into a 150-ml. beaker, with a 10-ml. pipet, made neutral to litmus with powdered sodium carbonate, and treated with the anthranilic acid reagent. The determination is continued as directed under white metal alloys.

4. Enamel Coating of Tin Cans

The enamel film is removed from a disk having an area of about two square inches, or the disk is cut into two 1-square-inch pieces and one of them is used for the determination. The film weight is obtained by weighing the section before and after removal of the film. The sample is immersed in chloroform in a 50-ml. beaker for rapid removal of the enamel coating. The chloroform is evaporated cautiously to avoid loss of small portions of the film; 1 or 2 ml. concentrated sulfuric acid is added, the solution is heated over a small flame, and a few drops of Superoxol are introduced to destroy the organic matter. When cool, 10 ml. water and 0.10 to 0.20 g. sodium tartrate are added. After the salt has dissolved, the determination is continued as described in the other procedures.

C. Other Methods for Zinc

A method for the determination of zinc after separation from cobalt, nickel, and manganese has been reported.[7] The zinc is first precipitated as the sulfide from a solution buffered to *p*H 2–3. Coprecipitation of cobalt, manganese, and nickel is prevented by the use of acrolein.[8] The precipitate of zinc sulfide is dissolved in acid. After the solution has been boiled to expel hydrogen sulfide and neutralized, the zinc is precipitated with anthranilic acid in the manner described previously.

A method for the determination of zinc in Babbitt metal with anthranilic acid has also been reported.[9] After copper, tin, lead, and iron have been removed by the conventional methods, zinc is determined in the final solution by precipitation with anthranilic acid, in preference to the use of diammonium hydrogen phosphate. This method

[7] E. A. Ostroumov, *Zavodskaya Lab.*, **6**, 1058 (1937).
[8] J. R. Caldwell and H. V. Moyer, *J. Am. Chem. Soc.*, **57**, 2372, 2375 (1935).
[9] E. I. Fogel'son and Z. S. Golovleva, *Zavodskaya Lab.*, **7**, 857 (1938).

would appear to offer some advantages over the phosphate method, particularly from the standpoint of speed.

III. Determination of Cobalt[10]

The solution to be analyzed should contain no more than 100 mg. cobalt in 250 ml., and the *p*H should be 4.5 or higher. As sodium acetate tends to dissolve the precipitate, large amounts of that salt should be absent, as well as the other interfering ions noted earlier. After the solution has been heated to boiling, it is treated with 15–20 ml. of the anthranilic acid reagent, and the boiling is continued for 5 minutes. After standing for about 10 minutes, the precipitate is filtered, washed with cold, diluted (5:95) reagent and then with alcohol, and dried to constant weight at 105–110°C. The precipitate, $Co(C_7H_6NO_2)_2$, contains 17.80% cobalt.

This method may be used to determine the cobalt which remains in the filtrate after a nickel dimethyglyoxime precipitation.[11] Sulfuric acid is added to the filtrate, which is then evaporated until fumes of sulfur trioxide appear. After the solution has been diluted and the *p*H adjusted, the cobalt is precipitated with anthranilic acid in the manner described.

A micromethod for the gravimetric determination of cobalt exists, in which the general procedural details resemble those given for the macromethod.[12]

IV. Miscellaneous Determinations

Various other metals may be determined, in relatively pure solutions, by precipitation with anthranilic acid. In many cases there is no advantage obtained by the use of this reagent; preliminary separations which are not necessary with other reagents may be required.

Copper. Macrogravimetric,[10, 13] volumetric,[10] and micromethods[14] have been described for the determination of copper with anthranilic acid. Precipitation is made from a boiling solution which is neutral or weakly acidic; the precipitate is filtered hot and washed with hot, di-

[10] H. Funk and M. Ditt, *Z. anal. Chem.*, **93**, 241 (1933).
[11] M. Ishibashi and A. Tetsumoto, *J. Chem. Soc. Japan*, **56**, 1221, 1228, 1231 (1935).
[12] P. Wenger, C. Cimerman, and A. Corbaz, *Mikrochemie*, **27**, 85 (1939).
[13] D. Gunev, *Khimiya i Industriya*, **20**, 170 (1941); *Chem. Abstracts*, **37**, 5331 (1943).
[14] P. Wenger and Z. Besso, *Mikrochemie*, **29**, 240 (1941); *Chem. Abstracts*, **37**, 3367 (1943).

luted (2:100) reagent. The precipitate is dried to constant weight at 105–110°C. Copper anthranilate, $Cu(C_7H_6NO_2)_2$, contains 18.38% copper.

Lead. A method for the gravimetric determination of lead has been described,[15] in which the lead is precipitated from a cold, nearly neutral solution. The precipitate should stand for 1 hour before filtering; it is then washed with cold, diluted (2:100) reagent followed by alcohol, and dried at 105°C. The precipitate contains 43.23% lead. The method has been used for the final precipitation of lead in the procedure described on page 229.[16]

Manganese. The comparatively high solubility of manganese anthranilate renders it only moderately useful as a precipitation form. A comparatively high *p*H is required for precipitation, and an undesirable tendency for oxidation of the manganous ion exists under these conditions. The precipitation method[17] cannot be recommended for general use.

Mercury. Although mercury(II) forms an anthranilate that may be easily dried and weighed,[15] the solubility of the salt in water is too great to make the reaction useful in gravimetric analysis.

Nickel. Nickel is precipitated by anthranilic acid from solutions which have a *p*H of about 6–7. Precipitation should be made from a boiling solution; the precipitate is filtered hot, washed with hot diluted (2:100) reagent followed by alcohol, and dried at 105°C. The precipitate, $Ni(C_7H_6NO_2)_2$, contains 17.74% nickel.[10]

V. Similar Reagents

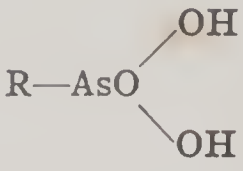
Shennan[18] has reported that 5-bromo-2-aminobenzoic acid may be used, in much the same manner as anthranilic acid, for the precipitation and determination of cobalt, copper, nickel, and zinc. The alkaline earths and alkali metals give no precipitates with the reagent, while most of the heavy metals do. An advantage of this reagent is its high molecular weight, although this may be offset somewhat by its lower solubility in water.

Finally, it has been reported[2] that 3-amino-2-naphthoic acid yields precipitates resembling the anthranilates, and that good results are obtained with it in the gravimetric determination of copper.

[15] H. Funk and F. Romer, *Z. anal. Chem.*, **101**, 85 (1935).
[16] C. Mahr and H. Ohle, *Z. anorg. Chem.*, **234**, 224 (1937).
[17] H. Funk and M. Demmel, *Z. anal. Chem.*, **96**, 385 (1934).
[18] R. J. Shennan, *J. Soc. Chem. Ind.*, **61**, 164 (1942).

CHAPTER VII

The Arsonic Acids



Name[a]	R	Molecular weight	Melting point, °C
Phenylarsonic acid	C_6H_5—	202.03	157–8
n-Propylarsonic acid	C_3H_7—	168.02	126–7
p-Hydroxyphenylarsonic acid	*p*-HOC_6H_4—	218.03	175–80
p-*n*-Butylphenylarsonic acid	*p*-$C_4H_9C_6H_4$—	258.13	—

[a] Solubility: soluble in water, alcohol.
Reagent solution: in water, 2.5 to 10% by weight, freshly prepared.

The investigation of these reagents has been due chiefly to Chandlee and co-workers, and has resulted in the development of a number of very useful methods. The reagents containing the arsonic acid grouping combine more or less preferentially with the quadrivalent metals, particularly the Group IV elements—tin, thorium, titanium, and zirconium. Other ions which yield insoluble salts with the reagents are: cerium(IV), hafnium, tungsten(VI), and uranium(IV). The tungstate ion may interfere, because tungstic acid precipitates under the conditions of moderately high acidity used for the precipitation of the quadrivalent metals. Iron(III) is precipitated quantitatively by *p*-*n*-butylphenylarsonic acid from a weakly acidic solution. With more strongly acidic solutions, *e.g.*, 1–2 *N* hydrochloric acid, precipitation is incomplete and may not occur at all if the amount of iron is small. The presence of fluoride, phosphate, tartrate, or citrate ions prevents the precipitation of iron under all conditions. The alkali metals, alkaline earths, transition elements, and most of the common heavy metals form no insoluble salts (at least in acidic solution) with the arsonic acids.

The arsonic acids are dibasic acids of moderate strength. A determination of the ionization constants of a number of these acids has

been made by Pressman and Brown.[1] In cases of aromatic and alkyl-substituted aromatic arsonic acids, K_1 is of the order of 10^{-4}, and K_2 of the order of 10^{-9}. Introduction of a nitro group into the aromatic nucleus in the meta or para positions increases both K_1 and K_2 by a factor of ten.

The insoluble salts of the arsonic acids with zirconium and titanium contain two moles of reagent for each atom of metal, and probably are hydrated in varying amounts. Since the quadrivalent forms of zirconium and titanium probably exist in solution as ZrO^{++} and TiO^{++}, the formation of an insoluble salt may involve bonding through the stronger of the acid functions in each of two molecules of precipitant. The other possibility, *i.e.*, that two molecules of dibasic acid react with one quadruply charged ion, seems less likely. Richter[2] suggests that the titanium salt of *p*-hydroxyphenylarsonic acid contains tetracovalent titanium, bound to the para hydroxyl and arsonic acid groups of each of two molecules of reagent. The steric difficulties involved are obvious. In any event, the composition of the precipitate is of minor importance for the analyst, since the precipitated element is eventually weighed as the more stable zirconium dioxide or titanium dioxide.

A large number of arsonic acids have been prepared and their reactions have been studied.[3] Naturally, some are more sensitive as qualitative reagents than others, but in general their reactions are similar. However, only the four compounds listed at the beginning of this chapter have found wide use in quantitative determinations.

The elements which may be determined advantageously by the arsonic acid reagents are: zirconium, titanium, thorium, iron, and tin. These will now be considered in detail.

I. Determination of Zirconium

A. With Phenylarsonic Acid[4]

The following procedure can be used for the determination of zirconium alone, or in the presence of aluminum, beryllium, bismuth, copper, iron(II), manganese(II), nickel, the trivalent rare earths, and zinc.

[1] D. Pressman and D. H. Brown, *J. Am. Chem. Soc.*, **65**, 540 (1943).
[2] F. Richter, *Z. anal. Chem.*, **121**, 1 (1941).
[3] F. Feigl, P. Krumholz, and E. Rajmann, *Mikrochemie*, **9**, 395 (1931).
[4] A. C. Rice, H. C. Fogg, and C. James, *J. Am. Chem. Soc.*, **48**, 895 (1926).

Zirconium should be in solution as the oxychloride, and the amount to be handled in a single determination should probably not exceed 300 mg. zirconium (as the dioxide). Sufficient hydrochloric acid should be present so that the final acid concentration, after dilution to 500 ml., will amount to 10% by volume. (Precipitation may also be made from a solution containing 10% sulfuric acid by volume. Higher concentrations of sulfuric acid lead to incomplete precipitation of the zirconium.) To the solution is added 10 ml. of the 10% phenylarsonic acid reagent; the mixture is boiled for about a minute and filtered hot. The precipitate is washed with hot 1% hydrochloric acid, dried, and ignited carefully in a good hood. The residue is reduced by heating in a stream of hydrogen, and then ignited to form zirconium dioxide over a strong flame. The precipitate of zirconium dioxide contains 74.03% zirconium.

B. In the Presence of Iron(III)[4]

Case 1. Zirconium Exceeding Iron. When there is a very much smaller quantity of iron than zirconium, the latter is separated as described in the preceding paragraph (precipitated in 10% hydrochloric acid and washed with 5% hydrochloric acid).

Case 2. Iron and Zirconium in Equal Amounts. Zirconium is precipitated as described above. Precipitate and paper are returned to the beaker and digested with 1:1 hydrochloric acid until the paper has disintegrated. The solution is then diluted to a volume of 500 ml., and 15 ml. of the precipitant is added; the mixture is boiled, filtered, washed, ignited, and weighed as above (see A).

Case 3. Iron Exceeding Zirconium (Twentyfold Excess). Zirconium is precipitated as above. The precipitate and paper are returned to the original beaker, treated with 15 ml. 1:1 sulfuric acid, and warmed until the zirconium has dissolved, after which 50 ml. hydrochloric acid (sp. gr. 1.18) is added. The solution is diluted to 500 ml., boiled, and treated with 30 ml. phenylarsonic acid. The determination is concluded in the usual manner.

C. In the Presence of Thorium[4]

Approximately equal quantities, of the order of 100 mg., of zirconium and thorium are separable by the procedures outlined in Cases 2 and 3.

D. In the Presence of Titanium[4]

The elements in roughly equal proportions should be dissolved in 500 ml. of approximately 10% hydrochloric acid. To the solution is added 35 ml. 3% hydrogen peroxide, followed by 30 ml. phenylarsonic acid reagent (for about 100 mg. zirconium); the mixture is thoroughly stirred, heated to boiling, filtered, and the precipitate is washed.

The precipitate is dissolved in 20 ml. 1:1 sulfuric acid; 20 ml. hydrogen peroxide and 50 ml. hydrochloric acid are added; the solution is diluted to 500 ml. and the zirconium is reprecipitated with 20 ml. phenylarsonic acid. The determination is concluded as outlined on page 109.

E. With *n*-Propylarsonic Acid[5]

With *n*-propylarsonic acid, zirconium is determined in the presence of numerous elements: aluminum, beryllium, cadmium, chromium, cobalt, copper, iron, magnesium, manganese, molybdenum, nickel, titanium, thorium, uranium, vanadium, and zinc, but not in the presence of antimony, bismuth, and tin.[6] The conditions of precipitation are the same as those which were used with phenylarsonic acid; an advantage in the use of the *n*-propylarsonic acid is the fact that the precipitate can be ignited directly to zirconium dioxide, first with a Bunsen burner, then with a Meker burner. Apparently, the arsenic volatilizes more readily from *n*-propylarsonic acid precipitate than from the corresponding phenylarsonic acid compounds, and preliminary ignition in hydrogen is unnecessary.

Presumably, the separations described for the determination of zirconium in the presence of iron(II), thorium, or titanium (pages 109–110) can be made with this reagent.

F. With *p*-Hydroxyphenylarsonic Acid[7, 8]

If this reagent is used in a hydrochloric acid solution not stronger than 3 *N* (or in sulfuric acid, 1.5 *N*), and if the general type of procedure described for the determination of zirconium with phenylarsonic acid (page 109) is followed, zirconium may be separated in a

[5] F. W. Arnold and G. C. Chandlee, *J. Am. Chem. Soc.*, **57**, 8 (1935).
[6] G. C. Chandlee, *J. Am. Chem. Soc.*, **57**, 591 (1935).
[7] C. T. Simpson and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **10**, 642 (1938).
[8] A. Claassen, *Rec. trav. chim.*, **61**, 299 (1942); *Chem. Zentr.*, **1942**, I, 3142.

single precipitation from copper, cadmium, vanadium, uranium, molybdenum, cerium, iron, aluminum, chromium, nickel, cobalt, zinc, manganese, and the alkaline earths. Reprecipitation is required when thorium is present.

Separation from titanium is made in 2.5 to 3.0 *N* sulfuric acid. A large excess of hydrogen peroxide, 15–20 ml. of a 30% solution, must be added to prevent titanium from precipitating; the wash liquid should also contain peroxide. An excess of precipitant somewhat greater than normal is also required: 3 g. of the reagent, instead of the usual 1 g., is required to give a quantitative separation of 100 mg. zirconium oxide in the presence of 50 mg. titanium dioxide.

When zirconium is being precipitated in the presence of iron, several grams of ammonium thiocyanate may be added to prevent interference by that element[7]; thiocyanate is also added to the wash liquid. It has been claimed[8] that the use of too much thiocyanate (more than 2–3 g. for a maximum of 100 mg. zirconium dioxide) causes incomplete precipitation of the zirconium.

Determinations with *p*-hydroxyphenylarsonic acid are concluded by heating in hydrogen followed by igniting,[8] or by igniting directly to zirconium dioxide.[7]

G. In Steel

1. With Phenylarsonic Acid[9]

A 5-g. sample of the steel is dissolved in 50–100 ml. 1:1 hydrochloric acid, to which a few drops of nitric acid have been added. After cooling, the solution is transferred to a separatory funnel and the iron is extracted with an equal volume of ether saturated with hydrochloric acid (see page 212). Complete removal of the iron is not essential. The residual ether is removed by heating; the solution is diluted to 500 ml., and 50 ml. hydrochloric acid (sp. gr. 1.18) is added. After addition of 50 ml. 3% hydrogen peroxide, the solution is treated with 10 ml. 2.5% phenylarsonic acid solution, and heated to boiling for several minutes. The precipitate is filtered hot, washed with 1% hydrochloric acid, and ignited in a hood with good draft. To remove silica, the precipitate is transferred to a platinum crucible and treated with 1 ml. hydrofluoric acid and 2 drops sulfuric acid. The crucible is heated carefully until fumes cease to be evolved, and then is heated vigorously. The residue is weighed as zirconium dioxide, which contains 74.03% zirconium.

[9] P. Klinger and O. Schliessmann, *Arch. Eisenhüttenw.*, **7**, 113 (1933).

Any insoluble material obtained upon initial treatment of the steel with hydrochloric acid is filtered, washed with hydrochloric acid (the washings are combined with the original solution), and ignited. The precipitate is fused first with sodium carbonate, and then with potassium pyrosulfate. Any zirconium thus obtained is precipitated in 10% hydrochloric acid, as above, and combined with the main precipitate.

2. With n-Propylarsonic Acid[10]

By this method, zirconium can be determined in a variety of steels if it is present in amounts as low as 0.1%. A small amount of iron is entrained by the initial precipitate, but reprecipitation overcomes this difficulty. Tin is partially precipitated by the reagent under the conditions used, but may be removed from the final zirconium dioxide precipitate by ignition with ammonium iodide. Other elements, such as titanium, aluminum, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum, and tungsten, are said to cause no interference. A particular advantage in the use of *n*-propylarsonic acid is the fact that it does not precipitate titanium.

A 3-g. sample of steel is dissolved in 40 ml. hydrochloric acid (sp. gr. 1.18), plus a few milliliters of nitric acid (sp. gr. 1.42), to oxidize the iron. The solution is evaporated to dryness; the residue is moistened with hydrochloric acid (sp. gr. 1.18), evaporated again, and baked for 30 minutes at 105–110° C. The residue is taken up by warming with 10 ml. hydrochloric acid (sp. gr. 1.18); the resultant solution is diluted to 100 ml., filtered hot, and the residue is washed well with hot water. Filtrate and washings are reserved, and the residue is treated as follows.

The residue is ignited in a platinum crucible, and the silica is removed by treatment with hydrofluoric and sulfuric acids in the usual manner. The residue is fused with sodium carbonate, then extracted with hot water, filtered, and washed well with hot water. The filtrate is discarded. The residue is ignited in platinum, and then fused with a small amount of potassium pyrosulfate. This melt is extracted with water and a few drops of sulfuric acid, filtered, and washed with hot water; the filtrate is added to the main filtrate.

The combined filtrates are diluted to 300 ml. and heated to boiling. The zirconium is then precipitated by the addition of 40–50 ml. of a

[10] H. H. Geist and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **9**, 169 (1937).

5% water solution of *n*-propylarsonic acid. The precipitate is digested for 30 to 60 minutes, filtered hot, and washed with hot water.

The filter paper containing the precipitate is returned to the original beaker and treated with 10 ml. hydrochloric acid (sp. gr. 1.18). The solution is diluted to 100 ml. and the zirconium reprecipitated by the addition of 10 ml. *n*-propylarsonic acid solution. After it has digested for 30 minutes, the precipitate is filtered and washed as described above. The precipitate is ignited in a porcelain crucible over a Meker burner, and the zirconium is weighed as zirconium dioxide. Should tin be present, it may be removed from the zirconium dioxide by repeated ignitions with ammonium iodide[11] until constant weight is obtained.

H. With Methylarsonic Acid[12]

The sodium salt of methylarsonic acid may be used to precipitate zirconium, and to separate it from many common elements, in much the same manner as phenylarsonic acid is used. The reagent has been used successfully in the analysis of ferrozirconium (with preliminary extraction of the iron by ether), aluminum–zirconium, and copper–zirconium alloys. The reagent precipitates titanium, and the preliminary separation of zirconium from that element is made by precipitation of zirconium with ammonium hydroxide in the presence of peroxide. Precipitation of zirconium in the presence of tin(IV) is unsatisfactory, as the tin is coprecipitated.

In general, methylarsonic acid seems to offer no advantage, except that it is cheaper and more readily available (it is also used as a medicinal, Arrhenal), over the phenyl and propyl compounds. Furthermore, *n*-propylarsonic acid has the added advantage of making a clean-cut separation of zirconium from titanium.

II. Determination of Thorium[4, 13]

Phenylarsonic acid precipitates thorium quantitatively from acetic acid–ammonium acetate solution. Under the same conditions, cerium(III), neodymium, probably the other rare earths, and aluminum are known to give no interference. Titanium, zirconium, and hafnium are precipitated, as are probably many other ions, *e.g.*, Ce(IV), Sn(IV), etc. The principal advantage in using the reagent lies in the separation it affords of thorium from the rare earths.

[11] E. R. Caley and M. G. Burford, *Ind. Eng. Chem., Anal. Ed.*, **8**, 114 (1936).
[12] R. Chandelle, *Bull. soc. chim. Belg.*, **46**, 283, 423 (1937); **47**, 172 (1938).
[13] H. Grundmann, *Aluminium*, **24**, 105 (1942).

Thorium may be in solution as the chloride, sulfate, or nitrate. The acidity should be as low as possible; up to about 300 mg. thorium may be treated conveniently. After dilution (if necessary) to 350 ml., the solution is heated almost to boiling and 50 ml. 1% phenylarsonic acid is added, followed by the addition of 75 ml. glacial acetic acid and 5 g. ammonium acetate (in a small amount of water). The precipitate is filtered, washed, returned to the original beaker, dissolved in 30 ml. 1:1 hydrochloric acid, and the solution is then diluted to 300–400 ml. After the addition of 15 ml. glacial acetic acid, the thorium is reprecipitated with a few milliliters of phenylarsonic acid and a slight excess of ammonium acetate. The solution is boiled, filtered, and the precipitate is washed thoroughly with water.

The precipitate is redissolved in 30 ml. 1:1 hydrochloric acid; the paper is removed by filtration, and the filtrate is diluted to about 300 ml. The thorium is precipitated from a boiling solution by 5 g. oxalic acid. The precipitate is allowed to stand several hours (or overnight) before being filtered, washed, and ignited to thorium dioxide for weighing. The precipitate, ThO_2, contains 87.88% thorium. Reprecipitation of the thorium phenylarsonate is unnecessary when the rare earths are absent. Final precipitation of thorium as the oxalate is always necessary, since all the arsenic is not removed from the phenylarsonate by simple ignition.

The determination of thorium in monazite sand has been described.[4]

III. Determination of Titanium

By precipitation with *p*-hydroxyphenylarsonic acid, titanium(IV) may be separated from the following: aluminum, beryllium, calcium, cerium(III), chromium(III, VI), cobalt, iron(II, III), magnesium, manganese(II, VII), molybdenum(VI), nickel, thallium(III), uranium (VI), vanadium(IV), and zinc. In all of these cases except for iron, the quantity of foreign ion is of the same order of magnitude as the titanium, *i.e.*, generally not more than 100 mg. Thorium causes no interference, provided that 6 g. of precipitant is used in place of the usual 4 g., and that the solution contains sulfuric rather than hydrochloric acid.

A. Basic Method

The sample containing not more than 60 mg. titanium dioxide is dissolved in hydrochloric or sulfuric acid, and interfering elements are

removed as required. The amount of acid present should be such that, after adding the necessary reagents, the solution will be no more than 0.6 *N* in hydrochloric, or 1.8 *N* in sulfuric, acid. The volume is adjusted to 200 ml.; the solution is then heated to boiling and 100 ml. 4% aqueous *p*-hydroxyphenylarsonic acid is added. If iron is present, 2 to 3 g. ammonium thiocyanate must be added before precipitation. The solution is boiled for 15 minutes; after it has been cooled to room temperature, the precipitate is filtered.

The precipitate is washed with 5 or 6 portions of 0.25 *N* hydrochloric (or sulfuric) acid containing 0.5 g. of the reagent per 100 ml. If iron is present, the wash solution should also contain 1 or 2 g. ammonium thiocyanate per 100 ml. The precipitate is finally washed with 2% ammonium nitrate, then dried, and ignited in a porcelain crucible (first at low, then at high, temperature) until the weight is constant. The ignition must be carried out in an efficient hood. The precipitate of titanium dioxide contains 59.95% titanium.

B. In Steel and Iron Ore

A 2- to 5-g. sample is taken, the weight depending on the amount of titanium present. After the sample has been dissolved in hydrochloric acid, silica is removed in the usual way. In the case of iron ore, the residue which is insoluble in hydrochloric acid is fused with sodium carbonate; the melt is washed into the main filtrate and the silica is removed. Five grams of ammonium thiocyanate is added; the solution is diluted to 300 ml. and titanium is precipitated with 100 ml. 4% aqueous *p*-hydroxyphenylarsonic acid in the manner described previously. The determination is concluded in the usual way.

C. Titanium and Zirconium in Burnt Refractory

A 2-g. sample is fused with 15 g. potassium pyrosulfate, and the melt is taken up in 100 ml. water containing 9 ml. sulfuric acid (sp. gr. 1.8). The residue is filtered off, and the silica is volatilized by heating with a mixture of sulfuric and hydrofluoric acids in a platinum dish. Any small remaining residue is fused with a little pyrosulfate and dissolved in the original filtrate. The solution is filtered, diluted to about 225 ml., and 2 g. ammonium thiocyanate is added. The determination is concluded in the manner previously described. The mixed titanium–zirconium oxide precipitate may be analyzed for zirconium;

the precipitate is first dissolved and then the zirconium is precipitated with *n*-propylarsonic acid (see page 110).

D. Titanium and Zirconium in Plastic Clay

A 2-g. sample is fused with sodium carbonate, taken up with dilute hydrochloric acid, and evaporated to dryness on a steam bath. The residue is extracted with dilute hydrochloric acid; the insoluble material is filtered off and evaporated to dryness in platinum with a mixture of sulfuric and hydrofluoric acids. Any remaining residue is again fused with sodium carbonate; the melt is dissolved in the original filtrate, and ammonia is added to neutralize most of the acid. Two g. of ammonium thiocyanate is added, and titanium is precipitated in the usual manner. For the separation of zirconium and titanium, see page 110.

E. Titanium and Zirconium in Titaniferous Materials

This method, which has been applied to the analysis of rutile, ilmenite, and calcium titanate, follows the same general lines as those already given. A 1-g. sample is fused for 1–2 hours with 20 g. potassium pyrosulfate at dark red heat, and care is taken to avoid decomposition of the pyrosulfate during the process. The cooled melt is treated with 200 ml. 1:5 sulfuric acid, and the silica is filtered off on a tough paper. The silica is ignited, fumed with sulfuric and hydrofluoric acids; any residue is fused with pyrosulfate and added to the main filtrate. As an alternative procedure, the silica may be fused with sodium carbonate–borax mixture, the cooled melt disintegrated with hydrochloric acid, the solution filtered, and the filtrate added to the main filtrate.

The main solution is treated with a few crystals of potassium chlorate (to oxidize iron) and diluted to 500 ml. in a volumetric flask. An aliquot of 150 ml. (0.3 g.) is taken for the determination of titanium. Aluminum, iron, and titanium are next precipitated with ammonium hydroxide; a double precipitation is necessary if calcium and magnesium are to be determined in the filtrate. The precipitate is washed well with ammonium nitrate solution, then with hot water. Filtrate and washings are combined for the determination of calcium as the oxalate, and magnesium as the hydroxyquinolate (see page 173). The precipitated oxides and hydroxides are dissolved in 70–80 ml. 1:1 hydrochloric acid; the solution is diluted to about 300 ml., and

titanium is precipitated in the usual manner. The use of 1 g. ammonium thiocyanate is recommended to keep the iron in solution.

IV. Determination of Iron with *p*-*n*-Butylphenylarsonic Acid[14]

Iron can be precipitated quantitatively from acidic solution with *p*-*n*-butylphenylarsonic acid, in the presence of a large number of ions, including: nickel, zinc, cobalt, manganese, copper, cadmium, aluminum, magnesium, calcium, potassium, beryllium, lanthanum, neodymium, erbium, and vanadium (as vanadate). Chromium (as chromate) interferes somewhat, but may be removed with one reprecipitation. Thallic salts cause no difficulty, provided that the precipitate is first washed with a saturated solution of the reagent in 1% hydrochloric acid, followed by water to remove chloride.

The precipitation of iron is prevented by tartrate, fluoride, citrate, or phosphate ions. Elements also precipitating with the reagent are: zirconium, thorium, titanium, tin(IV), uranium, and cerium.

The sample, which should contain no more than 70 mg. iron, is dissolved in nitric acid or aqua regia; the solution is diluted to 200 ml. and carefully neutralized with ammonia to the formation of the first permanent precipitate. Hydrochloric, nitric, or sulfuric acid is then added in sufficient quantity so that the solution after addition of the reagent, is approximately (but not more than) 0.4 *N*. The solution is heated almost to boiling, and 0.75 g. of the reagent dissolved in 100 ml. water at 80–90° is added slowly with stirring. After digestion for 20 minutes and cooling, the precipitate is washed first by decantation, then on a filter paper with warm 0.02 *N* hydrochloric acid, and finally with water until it is free from chloride.

The precipitate is ignited in a porcelain crucible over a low flame at first, and then heated strongly for half-hour intervals until constant weight is attained. The crucible should have a propped lid to insure complete volatilization of arsenic. The residue of ferric oxide, Fe_2O_3, contains 69.94% iron. This method has been used to determine iron in Monel metal and German silver.

V. Determination of Tin with Phenylarsonic Acid[15, 16]

This method offers no advantage over the conventional method of

[14] K. A. Craig and G. C. Chandlee, *J. Am. Chem. Soc.*, **56**, 1278 (1934).
[15] J. S. Knapper, K. A. Craig, and G. C. Chandlee, *J. Am. Chem. Soc.*, **55**, 3945 (1933).
[16] V. S. Suirokomskii and R. S. Pil'nik, *Zavodskaya Lab.*, **5**, 816 (1936).

determining tin by dehydration of metastannic acid and ignition to stannic oxide directly.

VI. Determination of Bismuth[17]

Bismuth may be precipitated quantitatively as the basic salt, $C_6H_5AsO_3BiOH$, at *p*H 5.1 to 5.3 from solutions buffered with sodium or ammonium acetate. Many other ions precipitate under similar conditions; however, since the cadmium, copper, cobalt, mercury(II), nickel, and silver phenylarsonates are soluble in potassium cyanide solution, bismuth can be separated from these elements. Furthermore, the precipitation of lead phenylarsonate may be prevented by a high concentration of ammonium acetate. Interference by aluminum, antimony, beryllium, chromium, iron, manganese(II), uranium(VI), and zinc cannot be avoided; these elements must be absent for the determination of bismuth by the phenylarsonic acid method. Thallium(I), the alkaline earths, and the alkali metals do not form precipitates under the conditions used for determining bismuth. Among the anions, nitrate and sulfate are without effect on the determination, but anions that form complexes with bismuth, such as citrate and tartrate, must be absent, as well as phosphate, arsenate, chloride, and fluoride.

The basic bismuth phenylarsonate may be dried and weighed, or dissolved in hydrochloric acid and analyzed iodimetrically. The gravimetric determination may be carried out on the microscale with milligram quantities of bismuth.

A. In the Absence of Interfering Ions

To a nitric acid solution containing up to 150 mg. bismuth, and free from the interfering substances listed above, is added an excess of the phenylarsonic acid reagent. The mixture is diluted to about 250 ml., and 10% sodium acetate is added until a precipitate forms; a slight excess does no harm. The *p*H should be 5.1 to 5.3. The solution is boiled and stirred until the initially gelatinous precipitate becomes crystalline. The boiling should not be prolonged, nor should a large excess of sodium acetate be present, since decomposition of the precipitate to form the oxide may occur. The precipitate is allowed to settle, filtered hot, and washed with 6 or 7 portions of hot water. Drying is carried out at 110–120°; the compound weighed, $C_6H_5AsO_3$-BiOH, contains 49.06% bismuth.

[17] A. K. Majumdar, *J. Indian Chem. Soc.*, **21**, 119, 187, 188 (1944); **22**, 313 (1945).

An alternative method of precipitation consists in the neutralization of the nitric acid solution containing bismuth and excess precipitant with 2 *N* ammonia until incipient precipitation occurs. The solution is then treated with 2 ml. 2 *N* acetic acid in excess of the amount required to acidify it; 20 ml. 10% ammonium acetate is also added. The mixture is diluted to 250 ml., heated to boiling, and the determination is continued as described previously.

This method of precipitation is used when sulfate ion is present; the solution is first freed of any precipitate by the addition of more nitric acid if necessary; then the solution is neutralized. Ammonium acetate buffer is also recommended for the separation of bismuth and lead. In this case, the addition of extra ammonium or sodium acetate may be desirable.

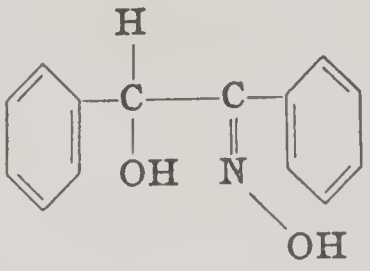
The volumetric analysis is carried out as follows: The washed precipitate of bismuth phenylarsonate is dissolved in the minimum amount of 1:1 hydrochloric acid and transferred to a flask. The solution is heated on a water bath for about 5 minutes; 2–3 g. potassium iodide is added, and the heating is continued for 10–15 minutes. The solution is cooled, 1–2 ml. starch indicator is added, and 0.1 *N* sodium thiosulfate is added dropwise until the blue color just disappears. After the addition of excess sodium bicarbonate, the solution is diluted to 200 ml., and titrated with standard iodine solution; 1 ml. 0.1 *N* iodine is equivalent to 10.45 mg. bismuth.

B. Separation of Bismuth from Cadmium, Cobalt, Copper, Nickel, and Silver

To the nitric acid solution containing bismuth and any of the above cations is added an excess of phenylarsonic acid. The solution is neutralized with dilute ammonia and sufficient potassium cyanide is added to keep the other cations in solution. The mixture is acidified with dilute acetic acid; an excess of 2 ml. is added along with 10 ml. 10% ammonium acetate. The solution is diluted to 250 ml., and the determination is continued as previously described.

CHAPTER VIII

α-Benzoin Oxime



Molecular weight: 227.3
Melting point: 149–151°C.
Solubility: soluble in alcohol, acetone, ether; insoluble in water
Reagent solution: 1 or 2% in 95% ethyl alcohol, stable for long periods of time

Insoluble compounds which are useful in connection with the quantitative precipitation and determination of these substances, are formed by α-benzoin oxime with copper, molybdate, and tungstate ions. The general manner in which this type of organic reagent combines with inorganic ions has been described in Chapter I.

Copper is precipitated from ammoniacal solution as a green, flocculent compound. The precipitate is insoluble in dilute ammonia, alcohol, and in the presence of tartrate ions, but dissolves in mineral acids, concentrated ammonia, or chloroform.[1] The insolubility of the copper complex in ammoniacal tartrate serves to separate copper from elements such as aluminum, cadmium, cobalt, iron, lead, nickel, and zinc.

From strongly acidic solutions, α-benzoin oxime precipitates molybdate and tungstate ions quantitatively.[2] Other ions precipitated wholly or partially under the same conditions include chromate, columbate, palladium(II), tantalate, and vanadate. Silica will also precipitate under much the same conditions.[3] However, in acid solution the number of elements that do not form precipitates is large; hence some useful separations are possible. Elements not precipitating

[1] I. M. Korenman and L. E. Ditsent, *Zavodskaya Lab.*, **10**, 493 (1941).
[2] H. Yagoda and H. A. Fales, *J. Am. Chem. Soc.*, **60**, 640 (1938).
[3] H. B. Knowles, *J. Research Natl. Bur. Standards*, **9**, 1 (1932).

with α-benzoin oxime in acidic solutions include: aluminum, antimony(III, V), arsenic(III, V), bismuth, cadmium, cerium(III), chromium(III), cobalt, copper, indium, iron(II,III), lead, manganese(II), mercury(I,II), nickel, osmium, platinum(IV), rhenium(VII), rhodium, ruthenium, selenium, silver, tellurium, tin(II,IV), titanium, uranium(IV,VI), vanadium(IV), zinc, the alkali metals, and the alkaline earths.

As to the properties of the precipitates, it may be stated that the copper complex is of definite composition and is stable at 105–115°, at which temperature it is conventionally dried prior to weighing. The copper α-benzoin oxime precipitates may be analyzed volumetrically by dissolving the filtered and washed precipitate in acid, heating the solution to insure complete hydrolysis of the oxime, and oxidizing the liberated hydroxylamine either with ferric iron,[4] or with potassium bromate.[5] Both methods involve a second titration, either of the ferrous iron produced in the oxidation process, or of the excess potassium bromate.

For the rapid determination of a large number of samples, a volumetric method for concluding the analysis is highly desirable. Other advantages inherent in these methods, *e.g.*, the gain in sensitivity, are described in Chapter V (page 87).

Silverman[6] concludes the determination of copper in ferrotungsten, ferromolybdenum, calcium molybdate, and cast iron in a still different manner. Evidence of Azzalin[7] is cited, purporting to show that: (*1*) the precipitate of copper benzoin oxime contains excess reagent that cannot be washed away, (*2*) the complete removal of carbon by ignition is difficult, and (*3*) in the presence of foreign elements, the precipitate is contaminated with these elements. Consequently, it is suggested[6] that the final determination of copper be made by the short iodide method or by electrodeposition.

The molybdate complex must be ignited (to molybdic oxide, MoO_3) for final weighing. If desired, the α-benzoin oxime precipitate may be dissolved in ammonium hydroxide and the molybdenum precipitated as lead molybdate,[8] which is a suitable weighing form. The advantage claimed for this process is that the critical ignition of the

[4] J. Mironoff, *Bull. soc. chim. Belg.*, **45**, 1 (1936).
[5] N. H. Furman and J. F. Flagg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 738 (1940).
[6] L. Silverman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 343 (1940).
[7] E. Azzalin, *Ann. chim. applicata*, **15**, 373 (1925).
[8] C. Sterling and W. P. Spuhr, *Ind. Eng. Chem., Anal. Ed.*, **12**, 33 (1940).

molybdic oxide is avoided. Arrington and Rice[9] ignite the α-benzoin oxime precipitate to molybdic oxide, which is then dissolved, reduced in a Jones reductor, and titrated with standard oxidant.

I. Determination of Copper[10]

The solution to be analyzed should contain no more than 50 mg. copper. If aluminum, cobalt, iron, etc., are present, tartrate is added to prevent precipitation of the hydroxides. After the addition of sufficient dilute ammonia to produce the deep blue tetrammine cupric ion, 5–10 ml. in excess is introduced. After the solution has been heated nearly to boiling, 10 ml. of the 2% reagent is added for each 50 mg. copper, and the solution stirred to coagulate the green precipitate. The precipitate is collected on a filtering crucible (fine porosity) and washed with hot 1% ammonia. Any excess precipitant is then washed out with 2 or 3 small portions of hot alcohol. The alcohol is allowed to stand in the crucible for several minutes before it is drawn through. The precipitate is dried to constant weight at 105–110°C.; it contains 22.01% copper.

A. Volumetric Analysis of the Copper Precipitate

(1) The copper complex which has been precipitated, filtered, and washed as described above, is dissolved in 15–20 ml. hot 12 *N* sulfuric acid. Suction should not be applied until the precipitate has dissolved. The filtering crucible is washed well with hot water. The filtrate and washings are concentrated to 25–30 ml.; upon cooling, the benzoin separates out and is filtered and washed with warm water. The filtrate and washings are again concentrated to 25–30 ml., 50 ml. 4% ferric sulfate solution is added, and the solution is boiled for 5 minutes. The ferrous iron, produced by the reduction of the ferric sulfate by the hydroxylamine, is titrated immediately with standard permanganate; 1 ml. 0.1000 *N* potassium permanganate is equivalent to 0.003178 g. copper.

(2) The copper complex is precipitated, filtered, and washed as described above. It is then treated in the crucible with 25 ml. hydrochloric acid (sp. gr. 1.19) until it is dissolved. The solution is drawn into the flask or bottle in which the titration is to be made. The cru-

[9] C. E. Arrington and A. C. Rice, *U. S. Bur. Mines, Rept. Investigations*, 3441 (1939).

[10] F. Feigl, *Ber.*, **B56**, 2083 (1923).

cible is washed with 25 ml. warm water. If necessary, more acid and more water are used in a 1:1 ratio. The receiving vessel is then fitted with a stopper carrying a separatory funnel and a tube provided with a 5-cm. (2-inch) piece of rubber tubing and a pinch clamp. Before the stopper is inserted, the solution is boiled for 5–10 minutes and then cooled to room temperature. Standard potassium bromate sufficient to oxidize the hydroxylamine and leave an excess of 10–15 ml., is then added through the separatory funnel. If necessary, water may be added to reduce the acid concentration to 3–4 *N*.

After the solution has been mixed and has stood for 15 minutes, a measured excess of standard arsenious acid containing 1 to 2 drops methyl orange is placed in the separatory funnel, and the flask or bottle is cooled under a tap, so that a good part of the arsenite is drawn in when the stopcock of the funnel is opened. When, after shaking the vessel, the red color of the methyl orange persists, the remainder of the arsenite and the washings are allowed to flow in by opening the pinch clamp. The stopper and funnel are then removed, and the excess of arsenite is titrated with bromate, with the addition of more methyl orange is necessary. The most critical part of the procedure is the prevention of the escape of bromine by adding the arsenite to the closed system after the reaction has taken place. Total milliequivalents of bromate used, less milliequivalents of arsenite, gives milliequivalents of bromate consumed by the complex (or milliequivalents of copper). The milliequivalent weight of copper is 10.595.

B. Gravimetric Microdetermination of Copper

The use of α-benzoin oxime for the gravimetric determination of less than milligram quantities of copper in pure copper solution has been reported[11] and gives reliable results.

The general procedure for the gravimetric microdetermination of copper is as follows: The copper nitrate solution, free from interfering elements, is evaporated in a weighed porcelain crucible together with a filter stick. The residue is dissolved with 3 drops 5–6% nitric acid; 2 ml. water is added, followed by sufficient ammonia to produce a clear, deep-blue solution. To the solution is added 1 ml. 1% α-benzoin oxime reagent in alcohol for each 0.5 to 0.6 mg. copper oxide expected. The mixture is shaken, and is then heated for about 10 minutes on a water bath to coagulate the precipitate. A few drops of alcohol should

[11] F. Hecht and R. Reissner, *Mikrochemie*, **17**, 130 (1935).

be added during the heating to insure that the excess precipitant remains in solution.

The hot solution is filtered through the filter stick and washed twice with 1-ml. portions of hot 1% ammonia, twice with hot water, and once with hot alcohol. The precipitate is dried at 105–110°, then covered with 1–2 ml. hot 95% alcohol, and crushed to as fine a state as possible with the filter stick. After this the solution is warmed for about 5 minutes on the water bath, and filtered hot. The precipitate is washed once again with hot water and dried at 105–110° to constant weight.

The volumetric methods described on page 122 serve well for the semimicrodetermination of copper, and have the advantage of favorable titration factors. Applications of methods for the microdetermination of copper with α-benzoin oxime are found in papers describing the determination of copper in organic substances, tissues, etc.[12]

1. In Steel Containing Molybdenum and Vanadium[13]

A sample (2–5 g.) of the steel is heated with 50–100 ml. 10% sulfuric acid in a 600-ml. beaker until the reaction is complete. If vanadium is absent, the solution is diluted to 250 ml. and heated to boiling; 1 g. sodium thiosulfate dissolved in 10–50 ml. water is then added per gram of steel. The boiling is continued for 10–15 minutes, and the precipitate is allowed to settle. If vanadium is present, several crystals of potassium chlorate are dissolved in the sulfuric acid solution. The solution is then diluted to 400 ml. with hot water, saturated with hydrogen sulfide for 15 minutes, and the precipitate is allowed to settle.

The sulfide precipitate in either case is filtered through a thick filter with moderate suction, and the filter and beaker are washed several times with 1% sulfuric acid. The precipitate and filter are ignited in a quartz crucible; the residue is treated with 10 ml. hydrochloric acid and heated until solution is complete. This solution is transferred to a 400-ml. beaker, and 2–3 drops nitric acid is added, followed by an excess of ammonia. The solution is heated to boiling and filtered into a 600-ml. beaker; the precipitate is washed thoroughly with hot dilute ammonia. The filtrate is diluted with 250 ml. hot water, heated to boil-

[12] Z. Gruzewska and G. Roussel, *Compt. rend. soc. biol.*, **121**, 289 (1936); *Chem. Abstracts*, **30**, 3744 (1936); *Bull. soc. chim. biol.*, **20**, 365 (1938).
[13] H. A. Kar, *Ind. Eng. Chem., Anal. Ed.*, **7**, 193 (1935).

ing, and precipitated by the slow addition of 10–15 ml. 1% α-benzoin oxime reagent, with stirring. The solution is boiled for 1 minute; some filter pulp is added, and the mixture is filtered through a retentive ashless paper. The precipitate is washed 5–6 times with hot 3% ammonia; the paper and precipitate are ignited in a quartz crucible and weighed as CuO. A somewhat similar procedure has been reported for the determination of copper in high-duty cast iron containing molybdenum.[14]

2. In Tungsten Steels

A sample (2–5 g.) of steel is heated with 50 ml. concentrated hydrochloride acid in a 600-ml. beaker until it is completely dissolved; 5 ml. nitric acid is added, and the solution is evaporated to dryness. After the residue has cooled, 25 ml. hydrochloric acid is poured over, and the solution is heated to dissolve salts of iron, chromium, etc. Several crystals of potassium chlorate are added and the solution is again heated to precipitate tungstic acid. The precipitate is allowed to settle, then filtered, and washed 10 times with cold 5% hydrochloric acid; 10–25 g. citric acid is added to the filtrate, which is then made (just) alkaline with ammonia. It is then acidified with hydrochloric acid, and 2 ml. in excess is added for each 100 ml. solution. The solution is heated to boiling and saturated with hydrogen sulfide. The precipitate is filtered and treated as described on page 125.

3. In Ferromolybdenum, Ferrotungsten, Ingot Iron, and Calcium Molybdate[6]

Preparation of Sample. For analyses in which silicon is also to be determined, 1 g. of the sample is weighed out, placed in a tall 300-ml. beaker, and treated with 20 ml. 1:2 nitric acid. After rapid action ceases, the beaker is heated until solution of the sample is about complete, is cooled somewhat, and 10 ml. concentrated sulfuric acid is added cautiously. The beaker is placed in a bumping beaker, and heated until heavy fumes of sulfuric acid are evolved. The mixture is cooled, and 75 ml. 1:4 hydrochloric acid is added; it is then heated until soluble salts are dissolved, and filtered at once. The precipitate is washed alternately with cold 1:4 hydrochloric acid and water 6 times, and then with hot solutions to remove the iron completely. The filtrate is used for the determination of copper. If silicon is not to be

[14] J. Stott, *Foundry Trade J.*, **63**, 128 (1940).

determined, the above nitric acid mixture is completely dissolved with the aid of some hydrofluoric acid. After the solution has been cooled and diluted with water, 10 ml. hydrochloric acid is added.

For molybdenum steels, the nitric acid solution method may be followed by fuming with perchloric acid. After the solution is cooled, water and hydrochloric acid are added. For calcium molybdate, 25 ml. 2:1 hydrochloric acid is used. For ferrotungsten, the sample is dissolved by the addition of 10 ml. 1:4 nitric acid and 5 ml. hydrochloric acid, and finally hydrofluoric acid is added dropwise to complete solution.

Precipitation of Copper. The prepared solutions are diluted to about 150 to 200 ml., and 15 g. Rochelle salt dissolved in 15 ml. water is added. A strong solution of sodium hydroxide is added until the test solution is alkaline to Congo red paper, but still acid to litmus paper; if necessary, it should be allowed to cool to room temperature. Ammonium hydroxide is added until the solution turns blue (copper about 0.5%), or until it is distinctly alkaline to litmus, and then about 5 ml. in excess is introduced. A 2% α-benzoin oxime solution (10 ml. for less than 0.5%, 15 ml. for 0.5 to 1.5% copper) is added slowly with stirring. The mixture is allowed to stand for about 15 minutes; the green precipitate is then filtered off on an 11-cm. Whatman No. 40 paper, and washed with warm (1:99) ammonium hydroxide solution.

Determination of Copper. The paper and contents are returned to the beaker, and 15 ml. nitric acid (sp. gr. 1.4) and 10 ml. perchloric acid (60 or 70% grade) are added. The mixed acid solution is heated until the nitric acid has been driven out and the perchloric acid condenses on the walls of the beaker. The solution is then cooled, diluted with water, and boiled until the chlorine has been driven off. (The short iodide titration for copper may be used from this point on.) Ammonium hydroxide is added until the solution is blue; the color is discharged with nitric acid, 4 cc. 1:1 sulfuric acid is introduced, and the copper is plated at 3 volts and 0.5 amperes.

Short Iodide Titration. If the short iodide titration for copper is used, ammonium hydroxide is added until the solution is just blue, then 2 g. solid ammonium bifluoride is added. When the salt has dissolved, 3 g. potassium iodide is added; the solution is then shaken and titrated with standard thiosulfate until the brown color due to the iodine has changed to a light yellow. After 2 ml. starch solution is added, the titration is continued until the blue color nearly disap-

pears. At that point 2 or 3 g. ammonium thiocyanate is added and the titration is completed.

Silverman[6] notes that the usual methods for separating copper from ferromolybdenum require separation from the molybdenum by the use of caustic (or by a fusion process), followed by separation of the copper from the iron; however, the method given accomplishes the separation of copper from these elements in a single step. He also points out that by Kar's method[13] copper and molybdenum are separated from the steel with thiosulfate, the sulfide precipitate is ignited to form the oxides which are then dissolved, and the copper is separated with α-benzoin oxime. In Silverman's method the separation is made directly.

Finally, Silverman notes that a satisfactory analysis for copper may be obtained if the steel is attacked with dilute sulfuric acid, the copper and molybdenum are precipitated with thiosulfate, the precipitate is fumed with nitric and perchloric acids, and the copper is electroplated. No comparative analyses are available to show whether the use of α-benzoin oxime is actually necessary.

C. Amperometric Titration of Copper with α-Benzoin Oxime[15]

Copper may be determined by amperometric titration with a solution of α-benzoin oxime. At applied potentials of between −0.8 and −1.4 v., and in the presence of gelatin as maximum suppressor, the L-shaped titration curve is obtained. At more negative potentials, up to about −1.9 v., the V-shaped titration curves are obtained. The reason for this is the appearance, at the higher potentials, of a second wave in the polarogram of α-benzoin oxime.

In either case, the best results are obtained in a supporting solution of 0.1 *M* ammonium chloride which is between 0.01 and 0.05 *M* with respect to ammonia. Higher concentrations of ammonia cause the points to be scattered and the titration curves to deviate from straight lines, thus making location of the end point by the tangent method difficult. This effect is presumably related to the solubility of the copper complex in ammonia.

The titrating solution is 0.01 *M* α-benzoin oxime in 50% alcohol prepared by direct weighing. The amount of copper determined should be of the order of 2 mg. per 50 ml. solution, and several drops of 10%

[15] A. Langer, *Ind. Eng. Chem., Anal. Ed.*, 14, 283 (1942).

gelatin solution should be present as maximum suppressor. Under these conditions the results are said to be accurate to within about ±1%.

The amperometric titration of microgram quantities of copper has also been reported.[16]

II. Determination of Molybdenum[3]

A. General Procedures

A solution containing not more than 0.15 g. hexavalent molybdenum and 10 ml. sulfuric acid (sp. gr. 1.84) in 200 ml. is prepared. If vanadates or chromates are present, sufficient sulfurous acid is added to reduce both; then the solution is boiled, and the boiling continued until the odor of sulfur dioxide can no longer be detected. The solution is next cooled to 5–10°, and 10 ml. 2% alcoholic α-benzoin oxime solution, plus 5 ml. extra for each 0.01 g. molybdenum, is added slowly with stirring. The stirring is continued, and bromine water, sufficient to tint the solution pale yellow, is added, followed by 5 ml. more of the reagent. The solution is kept at 5–10°C. for 15 minutes, stirred occasionally, and a little filter paper pulp is added. The precipitate is filtered on a retentive paper (S and S No. 589 Blue Band; Whatman No. 40), and washed with a solution containing 200 ml. sulfuric acid (sp. gr. 1.84) per liter. If sufficient reagent has been employed, the filtrate will deposit needlelike crystals on standing. The washed precipitate is transferred to a platinum crucible, slowly charred over a very low flame, and ignited to constant weight (preferably in an electric muffle furnace) at 500–525°C.

This method may be adapted for the analysis of cast iron[17] and other ferrous alloys.[18–20] A 1- to 5-g. sample of the material is dissolved in acid (perchloric, hydrochloric, nitric, sulfuric, or mixtures of these) and molybdenum is precipitated from the homogeneous sample.

When tungsten accompanies molybdenum, provision must be made for the separation of these elements. One very satisfactory method[3] consists in precipitating both tungsten and molybdenum with the aid of α-benzoin oxime, thus separating them from the other metallic con-

[16] J. T. Stock and M. A. Fill, *Metallurgia*, 30, 277 (1944).
[17] E. Taylor-Austin, *Analyst*, 62, 107 (1937).
[18] S. D. Steele, *Iron Steel Ind.*, 11, 267 (1938).
[19] W. W. Clark, *Chemist-Analyst*, 29, 83, 86 (1940).
[20] P. C. Baker, *ibid.*, 30, 31 (1941).

stituents. The precipitate is then ignited to form the mixed oxides, which are dissolved, and the molybdenum is precipitated as the sulfide from a buffered formic acid solution. The molybdenum is weighed, eventually, as the oxide or as thallous molybdate; the same applies to tungsten. Use of the thallium salts as weighing forms is recommended for the gravimetric determination of small amounts of molybdenum or tungsten.

Another manner in which tungsten and molybdenum may be separated is illustrated in the following section.

B. In Molybdenite and Wulfenite[3]

The ore is decomposed by treatment with nitric acid (sp. gr. 1.42) and bromine. It is then treated with 25 ml. 1:1 sulfuric acid and evaporated until fumes of sulfur trioxide appear. After the careful addition of 100 ml. water, the solution is heated to dissolve soluble sulfates, filtered, and the residue is washed with diluted (2:100) sulfuric acid. The small amounts of molybdenum retained in the residue may be determined colorimetrically. The filtrate is diluted to 200 ml., and the molybdenum is oxidized with 0.1 *N* potassium permanganate until a pink color persists in the solution. Fresh sulfurous acid solution is added to reduce chromium and vanadium, and the determination is continued as described in the preceding section.

Since the oxide obtained in the above process may be contaminated with tungsten, the following procedure should be used: The ignited oxide is dissolved in the minimum amount of warm, dilute ammonium hydroxide, and the residue is washed, filtered, and weighed. The extract containing the molybdenum is acidified with hydrochloric acid, treated with 5 ml. cinchonine reagent (125 g. cinchonine dissolved in 500 ml. concentrated hydrochloric acid and diluted to 1 liter). Some ashless filter paper pulp is added and the precipitate digested at 60–70°C. for 30 minutes, or overnight if desired. The tungstic acid precipitate is washed 3 times by decantation through an ashless filter paper; the wash solution is prepared by diluting 10 ml. of the cinchonine reagent to 1 liter with water. The precipitate is finally washed with several portions of 2% hydrochloric acid, dried, and ignited to constant weight at 570°C. The weight of the tungstic oxide plus that of the ammonia-insoluble material is deducted from the weight of the crude molybdic oxide.

C. In Cast Iron and Tungsten-Free Steel

1. Reagents Required

Nitric–Perchloric Acid Mixture. Three volumes of 68–70% technical grade perchloride acid is mixed with 1 volume of nitric acid (sp. gr. 1.42) and 1 volume of water.

Potassium Dichromate Solution. Potassium dichromate (1.4 g.) is dissolved in water and diluted to 100 ml.

Ferrous Sulfate, 5% Solution. Fifty grams ferrous ammonium sulfate hexahydrate is dissolved in water, 50 ml. 1:1 sulfuric acid is added, and the mixture is diluted to 1 liter.

α-Benzoin Oxime, 2% Solution. Two grams α-benzoin oxime is dissolved in 100 ml. ethyl alcohol.

Lead Acetate Buffer Mixture. Four grams lead acetate trihydrate is dissolved in a solution containing 275 ml. water, 550 ml. ammonium hydroxide (sp. gr. 0.90), 900 ml. 50% acetic acid, and 275 ml. hydrochloric acid (sp. gr. 1.19). The reagent is allowed to stand overnight and is then filtered.

2. Preparation of the Solution

The sample of steel or cast iron (3–5 g.) is transferred to a 600-ml. beaker, and 50 to 70 ml. nitric–perchloric acid mixture is added. The beaker is covered and heated gently until reaction ceases. After removal of the watch glass, 1 to 3 ml. hydrofluoric acid is added. Sufficient potassium chromate solution is added to cast iron samples to make the total chromium content of the solution at least 25 mg. The solution is evaporated from the open beaker until heavy white fumes appear; heating is continued until the volatile acids are driven from the beaker and the perchloric acid comes to a boil. The beaker is then covered and heated until the carbides and graphite are decomposed. It should be boiled gently to avoid excessive loss of perchloric acid.

The solution should be allowed to cool until the perchlorates crystallize; it is then diluted to 100 ml., stirred, and heated, if necessary, until the salts have dissolved. Any insoluble residue is filtered off.

3. Precipitation by α-Benzoin Oxime

After the prepared solution has been cooled to below 20°C., ferrous sulfate is added until the solution has a clear blue-green color which is not changed by the addition of a slight excess. It is diluted to 400 ml.

and cooled to 5–10° in an ice bath. Pieces of clean ice may be added to the solution itself.

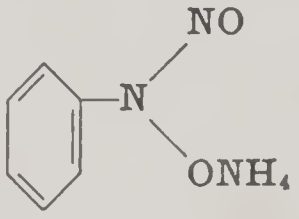
The following additions are made to the solution: 10 ml. α-benzoin oxime solution is added slowly with stirring; an additional 0.5 ml. is added for each milligram of molybdenum present; then bromine water is added with stirring until the solution is tinted a pale yellow; and finally 3–4 ml. more of the reagent is introduced. The mixture is allowed to stand for 5–10 minutes in the ice bath with occasional stirring. The precipitate is filtered on a 15-cm. rapid paper and washed with cold (2:98) sulfuric acid containing a few ml. of the reagent. The paper should be filled completely and allowed to drain before the cake is broken up with a stream from the wash bottle. The filtrate is treated with more reagent to insure complete precipitation of the molybdenum. Needlelike crystals will deposit on standing if sufficient excess reagent has been added.

4. Reprecipitation of Molybdenum as Lead Molybdate

The precipitate is transferred back to the original beaker by means of a jet of water; 10 ml. ammonia and 10 ml. 30% hydrogen peroxide are added. The mixture is diluted to 75 ml. and boiled until the evolution of oxygen ceases. It is filtered through the original paper, and the paper and small residue are washed with hot (2:98) ammonia. The hot ammoniacal solution, containing the molybdenum, is poured slowly with stirring into 100 ml. of boiling lead acetate buffer mixture, boiled gently until the precipitate coagulates, and allowed to settle for 30 minutes. If the precipitate is small, the settling period should be extended to several hours or overnight. The precipitate is filtered on a retentive paper containing a little paper pulp and washed thoroughly with hot 2% ammonium acetate solution containing a few ml. of acetic acid; the paper and residue are ignited in a porcelain crucible which is placed just inside a muffle furnace operating at a dull red heat. The crucible is ignited to constant weight, cooled, and weighed as lead molybdate, $PbMoO_4$, containing 26.14% molybdenum.

CHAPTER IX

Ammonium Nitrosophenylhydroxylamine (Cupferron)



Molecular weight: 155.15
Solubility: readily soluble in water
Reagent solution: 6% aqueous solution; addition of 50 mg. acetphenatidin per 100 ml. will stabilize for about one month, in daylight and at ordinary temperature,[1] otherwise solutions should be freshly prepared every few days. Cupferron (solid) should be stored in amber bottles containing a few lumps of ammonium carbonate.

The reactions of cupferron may be grouped into two classes: those taking place in strongly acidified solution, and those taking place in weakly acidic or neutral solution. Included in the first class would be the precipitation of cerium(IV), columbium, gallium, iron, tantalum, tin(IV), titanium, tungsten, uranium(IV), vanadium, zirconium, and probably hafnium. The elements precipitating in less acidic media include aluminum, bismuth, cerium(III), copper, lead, mercury, silver, and thorium, and probably many others as the *p*H increases. Precipitation may not be quantitative in the latter group of reactions. As the reagent is most useful when employed in strongly acid solutions—those containing 5–10% by volume of hydrochloric or sulfuric acid—only those reactions will be considered in this chapter.

The cupferron salts are presumably of the inner-complex type, but lack the characteristic stability so often encountered in these complexes. Consequently, cupferron complexes are always ignited before final weighings are made. Precipitation is generally made from a cold solution in order to prevent decomposition of the excess precipitant (into nitrobenzene), and of the precipitates themselves. No volumetric methods for analyzing cupferron precipitates have been developed.

[1] F. G. Germuth, *Chemist-Analyst*, **17**, 3 (1928).

Cupferron as a reagent for determining copper, aluminum, etc., is much less satisfactory than some of the other reagents such as 8-hydroxyquinoline, salicylaldoxime, or quinaldic acid, discussed elsewhere (Chapters XI, XVI, and XVII). The latter reagents offer advantages of greater selectivity as well as ease of handling and stability of the precipitate.

The solubilities of a number of cupferrides in aqueous solutions have been determined, and are given in Table XVIII.[2, 3] These are mostly

TABLE XVIII

Solubility of Cupferron Complexes in Aqueous Solutions

Element	Solubility (mg./liter) in water at 18°C.	Solubility (mole/liter)	
		1 *N* hydrochloric acid at 18°C.	0.01 *N* acetic acid
Aluminum	0.9	Soluble	
Antimony(III)	5.5	10^{-4}	
Bismuth	8.4	6×10^{-4}	
Cadmium	40.0	Soluble	5.46×10^{-3}
Chromium(III)	Soluble	Soluble	
Cobalt	77.0	Soluble	1.07×10^{-2}
Copper(II)	0.7	5×10^{-4}	1.3×10^{-4}
Iron(II)	0.02	2×10^{-4}	
Iron(III)	0.02	2×10^{-4}	
Lead	25.0	Soluble	
Manganese(II)	Soluble	Soluble	7.5×10^{-3}
Mercury(I)	0.3	Slightly soluble	
Mercury(II)	Soluble	Soluble	
Nickel	52.0	Soluble	1.06×10^{-2}
Silver	150.0	—	
Tin(IV)	2.4	10^{-4}	
Zinc	32.0	Soluble	6.3×10^{-3}

of interest in indicating the order of magnitude of the solubilities of the various complexes, and should be interpreted with reservations in view of the difficulties in measuring the solubilities of these rather unstable compounds. The columbium, copper, iron, tantalum, tin, thorium, uranium, and zirconium cupferrides are soluble in ether. This fact is often employed in concentrating small quantities of these cupferrides by extraction from acid solution.[4]

[2] A. Pinkus and F. Martin, *J. chim. phys.*, **24**, 83, 137 (1927).
[3] W. D. Treadwell and A. Ammann, *Helv. Chim. Acta*, **21**, 1249 (1938).
[4] O. Baudisch, *Arkiv. Kemi Mineral. Geol.*, **B12**, 6 (1936); *Brit. Chem. Abstracts*, **A1**, 48 (1937).

The following is a list of some of the useful determinations and separations that may be made with the aid of cupferron.

(*1*) The group separation of iron, titanium, vanadium, zirconium, etc., in strongly acidic solution from elements such as aluminum, arsenic, cobalt, copper, manganese, nickel, phosphorus, uranium(VI), alkaline earths, and alkali metals. Many possibilities for individual separations are afforded, such as the separation of (*a*) vanadium(V) from uranium(VI), (*b*) vanadium from phosphorus, (*c*) uranium(IV) from uranium(VI), (*d*) iron, etc., from pure metals such as aluminum and zinc, and (*e*) vanadium from tungsten, in the presence of fluoride.[5]

(*2*) Cupferron is often used for the removal of some undesired element. Thus, in the determination of aluminum in ferrochromium or chromium metal, iron is first removed by a cupferron precipitation, leaving a relatively clean solution for the determination of aluminum.[6] When determining phosphorus in ferrovanadium, cupferron may be used to advantage in removing both iron and vanadium prior to the determination of phosphorus, thus considerably simplifying the procedure for the determination of that element.

(*3*) Cupferron may be used to advantage on solutions which have been previously subjected to electrolysis with the mercury cathode. Elements such as bismuth, chromium, copper, iron, molybdenum, nickel, silver, tin, and zinc are quantitatively deposited in the mercury cathode, leaving aluminum, arsenic, phosphorus, titanium, uranium, vanadium, and zirconium in solution. Cupferron may then be used to separate titanium, vanadium, and zirconium from the others.[7, 8]

Lundell and Knowles,[9] on the basis of their own work and a critical survey of the published literature on the reagent up to that time (1920), draw the following conclusions, which remain largely valid, regarding the applications of cupferron in practical analysis: (*1*) Cupferron offers no advantages over (then) established procedures for the gravimetric determination of iron. Its primary value is in the separation of iron from other elements. (*2*) Cupferron offers no advantages as a reagent for copper, and the use of the reagent for determining

[5] S. G. Clarke, *Analyst*, **52**, 466, 527 (1927).
[6] T. R. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **3**, 103 (1931).
[7] W. R. Bennett, *J. Am. Chem. Soc.*, **56**, 277 (1934).
[8] A. M. Dymov and O. A. Valodina, *Zavodskaya Lab.*, **5**, 1047 (1936); *Chem. Abstracts*, **31**, 971 (1937).
[9] G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, **12**, 344 (1920).

copper has only theoretical interest. (*3*) Cupferron as a reagent for titanium and zirconium is of value mostly in enabling certain separations of these elements, as from aluminum and chromium. The arsonic acids more recently discovered offer greater advantages in the determination of these elements (see Chap. VII). (*4*) The determination of thorium by cupferron is no better than its determination by precipitation of that element by ammonia, and is subject to the same interferences. (*5*) The use of cupferron as a reagent for vanadium, *per se*, is of dubious value.

These authors emphasize the value of cupferron in making group separations, but caution against the many possible sources of interference, and suggest that the reagent be used only in cases where the qualitative composition of the sample is known, or where one is prepared to examine the cupferron precipitate quantitatively. A survey of cupferron, its uses and reactions, is contained in a monograph by Smith.[10]

A. Precipitation of Iron, Titanium, Vanadium, and Zirconium

The sulfuric or hydrochloric acid solution containing these elements should be free from silica, tungsten, tin(IV), uranium(IV), columbium, tantalum, molybdenum, and rare earths. The hydrogen sulfide group should be absent. Large amounts of phosphorus, alkaline earths, and alkali metals will contaminate the precipitate somewhat.

The solution is adjusted to about 200 ml. and sufficient sulfuric acid is added to make the solution about 10% acid by volume. Permanganate is added to insure complete oxidation of the elements. The solution is cooled to 10°C., and cold 6% cupferron solution is added slowly and with stirring until further addition produces a white silky precipitate of excess cupferron. The precipitate is filtered after 2 or 3 minutes, using a little filter pulp if increased bulk is required. The precipitate is collected on ashless paper and washed with cold 10% (by volume) sulfuric or hydrochloric acid containing 1.5 g. cupferron per liter.

If only iron is present, and it is to be determined, the precipitate is washed with 6 *N* ammonium hydroxide to remove excess precipitant and to convert the iron cupferride into ferric hydroxide. This is done

[10] G. F. Smith, *Cupferron and Neocupferron*. G. F. Smith Chemical Co., Columbus, Ohio, 1938.

to facilitate the final ignition, since removal of the organic matter lessens the chance for reduction of the iron during the ignition process. If the iron is not to be determined, or if other elements are present in the precipitate, the filter paper is dried in a platinum or porcelain crucible and the paper is carefully charred. The carbon is gradually burned off and the residue is finally ignited at the proper temperature for the oxides at hand. Copper may be removed from the cupferron precipitate by washing it with ammonia, in which the copper cupferride is soluble. It seems better, however, to remove copper first, along with the other hydrogen sulfide group elements, prior to the cupferron precipitation.

B. Precipitation and Determination of Tin

Tin(IV) is quantitatively precipitated by cupferron from a fluoboric acid solution, or any moderately acidic solution.[11–13] The value of being able to precipitate in the presence of fluoride lies in the fact that elements commonly associated with tin, such as antimony, arsenic, copper, and lead, may be quantitatively separated (as sulfides) from tin in fluoride solution. Furthermore, cupferron offers a convenient method of separating tin from other elements, such as aluminum and zinc, which would escape precipitation by hydrogen sulfide.

The preliminary precipitation of the hydrogen sulfide group occurs in about 0.5 *N* acid, with about 5 ml. 48% hydrofluoric acid also present. If antimony is present it must be in the trivalent form, and several grams of tartaric acid and sodium acetate must be added to the solution. Precipitation is made with a rapid stream of hydrogen sulfide. After filtering and washing the precipitate, the filtrate is treated with 4 g. boric acid, boiled to expel hydrogen sulfide, and concentrated if necessary to about 500 ml. No more than 300 mg. tin should be present. To the cold solution is added slowly an excess of 10% cupferron solution. The precipitate is allowed to stand for 30 to 45 minutes, and is then broken up with a stirring rod and filtered. After being washed with cold water and dried, the precipitate is ignited to the dioxide, SnO_2, containing 78.77% tin, for final weighing.

[11] A. Kling and A. Lassieur, *Compt. rend.*, **170**, 1112 (1920).
[12] N. H. Furman, *Ind. Eng. Chem.*, **15**, 1071 (1923).
[13] A. Pinkus and J. Claessens, *Bull. soc. chim. Belg.*, **31**, 413 (1927).

Iron, titanium, zirconium, etc., are not separated from tin by this procedure. A modified method for separating tin and antimony has been given.[14]

After oxidation of tin and antimony in chloride solution with hydrogen peroxide and decomposition of the excess peroxide by boiling, a slight excess of ammonia is added. Then 5% more than a twofold excess of cupferron is added, followed by 1 ml. 1% gelatin solution and a few drops of 2% tannin per 100 ml. of solution. The suspension is stirred, filtered, washed, and the precipitate is ignited to tin dioxide. A microseparation of tin and antimony has also been described,[15] using a similar procedure. In the analysis of nonferrous metals for tin, the tin may be separated from the other constituents by distillation as the tetrabromide. Cupferron is then used to precipitate and determine tin in the distillate.[16]

C. Precipitation and Determination of Uranium[17]

If uranium is to be determined in the filtrate from the iron group precipitation (page 136), the solution is evaporated to 50 ml.; 20 ml. nitric acid is added, and the evaporation is continued until fumes of sulfur trioxide appear (after adding sulfuric acid, if necessary). If organic matter remains, the treatment with nitric acid should be repeated. Care must be taken to expel all free nitric acid. The solution is diluted so that it contains about 6 ml. sulfuric acid per 100 ml.; it is then passed through a Jones reductor. The reduced solution, plus washings of 8% sulfuric acid, is cooled to 5–10°, and treated with excess cupferron reagent. Macerated paper is added and, after being allowed to settle for a few minutes, the precipitate is filtered and washed with a cold solution of 4% sulfuric acid containing 1.5 g. cupferron per liter. The precipitate is dried, then ignited at 1000°, cooled, and weighed as U_3O_8, which contains 84.8% uranium.

D. Miscellaneous Precipitations and Determinations

In this section methods are listed in which cupferron plays an important part. Many other cases in which the use of cupferron is more

[14] E. Gray, *Compt. rend.*, **212**, 904 (1941); *Chem. Abstracts*, **37**, 2298 (1943).
[15] M. von Mack and F. Hecht, *Mikrochim. Acta*, **2**, 227 (1937).
[16] W. D. Mogerman, *J. Research Natl. Bur. Standards*, **33**, 307 (1944).
[17] J. A. Holladay and T. R. Cunningham, *Trans. Am. Electrochem. Soc.*, **43**, 329 (1923).

or less incidental have been reported, but are not listed since they represent only additional applications of reactions already given.

Aluminum. The use of cupferron for the determination of aluminum seems to offer no real advantages. Methods have been given, but in most cases these offer no improvement over conventional precipitation methods, as for example, with ammonia.[18–22]

Bismuth. The bismuth cupferride forms in moderately acid solution of *p*H 0 or greater. The large number of interfering ions detracts from the usefulness of the reaction.[23, 24]

Copper. Numerous methods for separating and determining copper have been given. None possesses advantages over methods involving the precipitation of inner-complex salts that may be dried and weighed directly, however.[25–32] Copper may be determined by conductometric titration using a standard solution of cupferron. The method is useful in the analysis of brass and bronze, since no soluble constituents interfere and a direct determination is possible. The maximum error is 0.8% on 100 mg. of copper.[33]

Gallium. It is claimed that gallium is precipitated quantitatively from sulfuric acid solution, 2 *N* or weaker, and that under these conditions a separation from aluminum, chromium, and indium is effected. Iron must be removed previously by precipitation as ferrous sulfide from an alkaline tartrate solution.[34–37]

[18] A. Pinkus and E. Belche, *Bull. soc. chim. Belg.*, **36**, 277 (1927).
[19] L. DeBrouchere and E. Belche, *ibid.*, **36**, 288 (1927).
[20] P. Meunier, *Compt. rend.*, **199**, 1250 (1934).
[21] V. M. Zvenigorodskaya and Yu. Chernikov, *Zavodskaya Lab.*, **9**, 1089 (1940); *Chem. Abstracts*, **35**, 1342 (1941).
[22] M. G. Raeder and B. Lyshoel, *Kgl. Norske Videnskab. Selskab. Forh.*, **15**, 55 (1942); *Chem. Abstracts*, **38**, 1973 (1944).
[23] A. Pinkus and J. Dernies, *Bull. soc. chim. Belg.*, **37**, 278 (1928).
[24] E. A. Ostroumov, *Zavodskaya Lab.*, **4**, 1016 (1935); *Chem. Abstracts*, **30**, 1684 (1936).
[25] H. Biltz and O. Hodtke, *Z. anorg. Chem.*, **66**, 426 (1910).
[26] J. Hanus and A. Soukup, *ibid.*, **68**, 55 (1910).
[27] O. Baudisch, *Chem. Ztg.*, **35**, 913 (1911).
[28] R. Fresenius, *Z. anal. Chem.*, **50**, 35 (1911).
[29] H. Weber, *ibid.*, **50**, 50 (1911).
[30] O. Baudisch and V. L. King, *Ind. Eng. Chem.*, **3**, 629 (1911).
[31] N. Tscherwiakow and E. Ostroumov, *Ann. chim. anal. chim. appl.* **18**, 201 (1936).
[32] N. Ssurenkow, *Zavodskaya Lab.*, **2**, 17 (1933).
[33] J. F. Corwin and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 302 (1946).
[34] L. Moser and A. Brukl, *Monatsh.*, **51**, 325 (1929).
[35] A. Brukl, *ibid.*, **52**, 253 (1929).
[36] E. S. von Bergkampf, *Z. anal. Chem.*, **90**, 333 (1932).
[37] J. A. Scherrer, *J. Research Natl. Bur. Standards*, **15**, 585 (1935).

Iron. The precipitation, separation, and determination of iron follows the method outlined on page 136. Numerous studies have been made on the determination of iron, [25, 28, 30, 33–46]

Mercury. The large number of interfering elements detracts from the interest of this method.[47]

Tantalum and Columbium. These elements may be separated from iron by precipitation of that element with hydrogen sulfide in an ammonium oxalate–tartrate solution. From the filtrate tantalum and columbium are precipitated with cupferron.[48, 49] The use of cupferron to precipitate columbium, tantalum, and titanium in the mineral perovskite and its analogs has been reported.[50]

Titanium. The general procedure for the precipitation and determination of titanium has already been given (page 136). Methods dealing with special cases include: separation from iron, aluminum, uranium, phosphoric acid, etc.[51–55]; the analysis of ores such as rutile and ilmenite[7, 56, 57]; and the analysis of steel and related products.[58, 59]

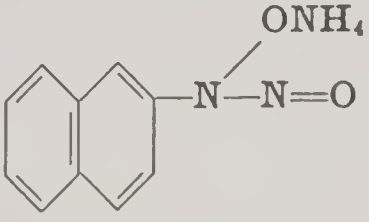
Thorium. Thorium is precipitated as $Th(C_6H_5(NO)NO)_4$ from acetic acid solution upon the addition of cupferron, together with many other elements. The practical value of cupferron in determining thorium is limited.[60, 61]

[38] O. Baudisch, *Chem. Ztg.*, **33**, 1298 (1909).
[39] H. Nissenson, *Z. angew. Chem.*, **23**, 969 (1910).
[40] K. Schroder, *Z. anorg. Chem.*, **72**, 89 (1911).
[41] F. Ferrari, *Ann. chim. applicata*, **4**, 341 (1915).
[42] E. H. Archibald and R. V. Fulton, *Trans. Roy. Soc. Can.*, **13**, 24 (1919).
[43] N. D. Ridsdale, *Chem. News*, **120**, 219 (1920).
[44] N. J. Matwejew, *Tsvetnye Metally*, **1**, 85 (1930).
[45] F. C. Mathers and C. E. Prichard, *Proc. Indiana Acad. Sci.*, **43**, 125 (1934).
[46] E. C. Pigott, *Ind. Chemist*, **11**, 273 (1935).
[47] A. Pinkus and M. Katzenstein, *Bull. soc. chim. Belg.*, **39**, 179 (1930).
[48] H. Pied, *Compt. rend.*, **179**, 897 (1924).
[49] T. R. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **10**, 233 (1938).
[50] B. N. Melent'ev and A. S. Terekhovo, *Trudy Kol'skoi Bazy Akad. Nauk S.S.S.R.*, **1940**, No. 5, 71; *Khim. Referat. Zhur*, **4**, No. 2, 60 (1941); *Chem. Abstracts*, **37**, 3019 (1943).
[51] I. Bellucci and L. Grassi, *Gazz. chim. ital.*, **43**, 570 (1913).
[52] W. M. Thornton, *Am. J. Sci.*, **37**, 173, 407 (1914); *Z. anorg. Chem.*, **87**, 375 (1914).
[53] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **42**, 1439 (1920).
[54] E. S. von Bergkampf, *Z. anal. Chem.*, **83**, 345 (1931).
[55] A. Angeletti, *Ann. chim. applicata*, **17**, 53 (1927).
[56] C. Mayr and A. Gebauer, *Z. anal. Chem.*, **113**, 189 (1938).
[57] J. Waddell, *Analyst*, **44**, 307 (1919).
[58] T. R. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **5**, 305 (1933).
[59] L. Silverman, *Chemist-Analyst*, **23**, No. 3, 4 (1934).
[60] W. M. Thornton, Jr., *Chem. News*, **114**, 13 (1916); *Am. J. Sci.*, **42**, 151 (1916).
[61] N. J. Matwejew, *J. Appl. Chem. (U.S.S.R.)*, **4**, 275 (1931).

Vanadium. The general conditions for precipitating and determining vanadium have been described on page 136. Some of the more important separations that may be made using cupferron are: vanadium from tungsten,[5] and from arsenic, phosphorus, and uranium[62]; also from miscellaneous elements.[63, 64]

Zirconium. Like titanium, zirconium is quantitatively precipitated by cupferron. Its use in the analysis of steel,[53, 65, 66] bauxite,[67] zircon,[68] and in making various separations as described on page 136 have been reported.[69, 70]

II. Ammonium Nitrosonaphthylhydroxylamine (Neocupferron)



This reagent has found use in precipitating and determining traces of iron and copper. The complexes are apparently less soluble than the corresponding cupferrides; consequently, it has been possible to determine iron and copper directly in natural waters without preliminary concentration.[71]

A. Determination of Iron and Copper in Water

To 500 ml. water is added 30 ml. hydrochloric acid (sp. gr. 1.18); the solution is cooled to 5–10°C. A tenfold excess of neocupferron (obtainable from G. F. Smith Chemical Co., Columbus, Ohio) is added, together with some macerated filter paper, and the precipitate is allowed to stand in the cold for one hour. The precipitate is then filtered and is washed first with ice water, then with 0.7 *N* hydro-

[62] W. A. Turner, *Am. J. Sci.*, **41**, 339 (1916); **42**, 109 (1916).
[63] V. G. Rodeja, *Anal. soc. espan. fis. quim.*, **12**, 305, 379 (1914).
[64] M. G. Raeder and T. Aakre, *Kgl. Norske Videnskab. Selskab. Forh.*, **15**, 75 (1942); *Chem. Abstracts*, **38**, 6232 (1944).
[65] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, **12**, 562 (1920).
[66] P. Klinger and O. Schliessmann, *Arch. Eisenhüttenw.*, **7**, 113 (1933).
[67] G. E. F. Lundell and J. I. Hoffman, *J. Research Natl. Bur. Standards*, **1**, 91 (1928).
[68] J. Brown, *J. Am. Chem. Soc.*, **39**, 2358 (1917).
[69] W. M. Thornton and E. M. Hayden, *Am. J. Sci.*, **38**, 137 (1914).
[70] A. Angeletti, *Gazz. chim. ital.*, **51**, 285 (1921).
[71] O. Baudisch and S. Holmes, *Z. anal. Chem.*, **119**, 241 (1940).

chloric acid, and then again with ice water. Copper may be removed from the precipitate by washing with 5 *N* ammonia. The precipitate is dried and ignited to ferric oxide.

CHAPTER X

The α-Dioximes ($R_2C_2N_2O_2H_2$)

Name[a]	R	Molecular Weight	Melting point, °C	Solubility
Dimethylglyoxime	CH_3—	116.1	237–8	Sol. alcohol, insol. water
Benzildioxime	C_6H_5—	240.2	235–7 (dec.)	Sol. alcohol, insol. water
Furildioxime	C_4H_3O—	220.2	164–8 (dec.)	Sol. water, alcohol

[a] Reagent solution: 1% in 95% ethanol, or 3% in 1 *N* sodium hydroxide; alcoholic solutions are stable indefinitely.

The value of this class of compounds in analytical chemistry has long been recognized.[1] Dimethylglyoxime and many other dioximes and related compounds possessing the so-called "nickel-specific" group have been studied, and much is known with regard to their general properties and behavior.[2] In this chapter will be given some of the more important analytical applications of dimethylglyoxime in the determination of nickel and palladium.

Dimethylglyoxime, as well as other α-dioximes, forms insoluble compounds with relatively few elements. Among these are nickel, palladium(II), platinum(II), iron(II), and bismuth. With many other ions, water-soluble complexes are formed. Precipitation of nickel from an ammoniacal tartrate solution serves to separate that element from a large number of elements with which it is commonly associated; therein lies one of the more important values of these reagents.

The bright red nickel dimethylglyoxime is insoluble in aqueous solutions of high *p*H. The optimum *p*H for precipitation is reported[3] as

[1] L. H. Tschugaeff, *Z. anorg. Chem.*, **46**, 144 (1905).

[2] For detailed discussions, see H. Diehl, *The Applications of the Dioximes to Analytical Chemistry*. G. F. Smith Chemical Co., Columbus, Ohio, 1940. Also, J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*. Wiley, New York, 1941. A brief discussion of these compounds is included in Chapter I, page 16.

[3] T. Nagai, *Compl. Abs. Jap. Chem. Lit.*, **6**, 409 (1932); *Brit. Chem. Abstracts*, **A**, 246 (1933).

being between 7.5 and 8.1. At *p*H 4.05 the solubility of the complex in an acetate buffer is about 9.5 mg. per liter, as determined polarographically.[4] At the higher *p*H ordinarily used in a precipitation, the solubility is undoubtedly much less. The solubility of the complex in various solutions, *p*H unknown, is given in Table XIX. The solubility

TABLE XIX

Solubility of Nickel Dimethylglyoxime[a]

Solute	Solubility, mg./100 ml.
Cold water	<0.1
Hot water	0.6
Hot water, 0.2 g. dimethylglyoxime	0.5
Hot water, 0.5 g. dimethylglyoxime	0.5
Hot water, 0.2 g. dimethylglyoxime, 150 ml. hot alcohol	1.5
Hot water, 0.2 g. dimethylglyoxime, 100 ml. hot alcohol	1.1
Hot water, 0.2 g. dimethylglyoxime, 50 ml. hot alcohol	0.8
Hot water, 0.2 g. dimethylglyoxime, 100 ml. cold alcohol	<0.1
Cold water, 2 g. sodium acetate, 50 ml. 0.1 *N* hydrochloric acid	<0.1
Hot water, 0.2 g. dimethylglyoxime, 2 g. sodium acetate, 20 ml. 0.1 *N* hydrochloric acid, 100 ml. hot alcohol	0.8
Hot water, 0.2 g. dimethylglyoxime, 2 g. sodium acetate, 20 ml. 1 *N* hydrochloric acid	0.5

[a] P. Nuka, *Z. anal. Chem.*, **91**, 29 (1932).

of the complex in alcohol has been noted by Nussbaumer[5]; chloroform is also a good solvent for nickel dimethylglyoxime, and solutions of the complex in that solvent are often used in colorimetric work. Mineral acids dissolve the nickel and bismuth complexes readily, but not the palladium or platinum complexes.

The nickel and palladium salts have uniform composition, and are easily dried at 110°. Occasionally the palladium complex is ignited to metallic palladium. The bismuth complex is always ignited to bismuth sesquioxide. Because the nickel salt sublimes at 250°, ignition is not recommended; the complex is dried at 110°C.

A minor disadvantage in the use of the dioxime reagents may be their insolubility in water. In the case of dimethylglyoxime this may be overcome by using the recently available sodium salt, $Na_2C_4H_6$-

[4] I. M. Kolthoff and A. Larger, *J. Am. Chem. Soc.*, **62**, 211 (1940).
[5] F. Nussbaumer, *Metallwirtschaft*, **20**, 599 (1941).

$O_2N_2 \cdot 9\ H_2O$ (from Tower Drug and Chemical Co., Rochester, N. Y.) or an alkaline solution of dimethylglyoxime. Alternatively, α-furil dioxime may replace dimethyglyoxime[6]; it is soluble in water and, with α-benzil dioxime,[7] listed at the beginning of this chapter, forms a complex with a more favorable conversion factor. 1,2-Cyclohexanedione dioxime has been suggested as a possible reagent for nickel.[8] In the following sections the use of dimethylglyoxime will be specified, with the understanding that in most instances it may probably be replaced with either of the afore-mentioned reagents.

I. Recommended Specifications for Dimethylglyoxime[9]

A. Requirements

Insoluble in alcohol: not more than 0.05%
Residue on ignition: not more than 0.05%
Suitability for nickel determination: to pass test

B. Tests

Insoluble in Alcohol. Gently boil 2 g. with 100 ml. ethyl alcohol under a reflux condenser until no more dissolves. Filter on a tared filtering crucible; wash with 50 ml. alcohol, and dry at 105–110°C. The weight of the insoluble residue should not exceed 0.0010 g.

Residue on Ignition. Ignite 1 g. at a temperature high enough to burn off the carbonaceous matter. Cool, add 1 drop sulfuric acid, and continue the ignition at dull redness for 5 minutes. The weight of the residue should not exceed 0.0005 g.

Suitability for Nickel Determination. Dissolve 1.00 g. nickel ammonium sulfate hexahydrate in exactly 50 ml. water. Dilute 20 ml. of this solution to 100 ml., heat to boiling, and add a solution of 0.25 g. of the dimethylglyoxime in 25 ml. alcohol. Add diluted ammonium hydroxide (1:4), drop by drop, to alkaline reaction; cool, and filter. Add to the filtrate 1 ml. nickel ammonium sulfate solution and heat to boiling. A substantial precipitate of nickel dimethylglyoxime should appear.

[6] B. A. Soule, *J. Am. Chem. Soc.*, **47**, 981 (1925).
[7] F. W. Atack, *Analyst*, **38**, 316 (1913).
[8] E. G. Rauh, G. F. Smith, C. V. Banks, and H. Diehl, *J. Org. Chem.*, **10**, 199 (1945).
[9] E. G. Wichers *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **16**, 281 (1944).

II. Determination of Nickel[10–18]

The determination of nickel presents no unusual difficulties. A few important points in connection with foreign elements may be mentioned: (*1*) Palladium, platinum, gold, and large amounts of copper, arsenic, molybdenum, etc. (hydrogen sulfide group elements), must be absent. Moderate amounts of the latter elements cause no trouble. (*2*) Small amounts of silicon and tungsten do not interfere. (*3*) Interference from iron and aluminum is prevented by use of tartrate or citrate salts. (*4*) When much cobalt, zinc, or manganese is present, the precipitation should take place in a sodium acetate, rather than an ammonium salt, buffer. (*5*) If appreciable amounts of cobalt, copper, or zinc are present, extra reagent should be added to combine with these ions. (*6*) When precipitating in the presence of the alkaline earths, zinc, magnesium, and manganese, carbonate-free reagents must be used, and the solution must contain ammonium salts; see (*4*), however. (*7*) The nickel precipitate may be analyzed volumetrically; in general, however, the gravimetric method is about as convenient, although less accurate for small amounts.

The precipitate is insoluble in dilute ammonia, in solutions of ammonium salts, in buffered acetate solution, and in excess reagent. It is readily soluble in mineral acids.

1. Precipitation in Ammonia Buffer

The solution to be analyzed should contain no more than 30 mg. nickel, and should be free from interfering elements (see above). Any iron must be in the trivalent condition (oxidized with bromine water and excess oxidant removed by boiling). Sufficient mineral acid should be present to provide 1–2 g. of ammonium salts when the solution is neutralized. If iron, aluminum, etc., are present, 1 g. tartaric acid should also be added.

The solution is diluted to 200 ml., heated almost to boiling, and a slight excess of ammonia (sp. gr. 0.90) is added. If a precipitate ap-

[10] O. Bruncke, *Z. angew. Chem.*, **20**, 834, 1844 (1907); *ibid.*, **27**, 315 (1914).
[11] H. Weber, *Z. anal. Chem.*, **47**, 162 (1908).
[12] K. Wagenmann, *Z. angew. Chem.*, **28**, 590 (1915).
[13] H. Grossmann and J. Mannheim, *ibid.*, **30**, 159 (1917).
[14] S. Rothschild, *Chem. Ztg.*, **41**, 29 (1917).
[15] L. A. Congdon and C. H. Belge, *Chem. News*, **128**, 67 (1924).
[16] J. G. Weeldenberg, *Rec. trav. chim.*, **43**, 465 (1924).
[17] F. Feigl and H. J. Kapulitzas, *Z. anal. Chem.*, **82**, 417 (1930).
[18] M. Ishibashi and A. Tetsumoto, *J. Chem. Soc. Japan*, **56**, 1221, 1228 (1935).

pears, the solution is acidified and more tartaric acid, followed by more ammonia, is added. When the solution remains clear at this point, it is acidified with hydrochloric acid and 5 ml. 1% dimethylglyoxime reagent is added for each 10 mg. of nickel present. Dilute ammonium hydroxide is added until precipitation occurs; then a slight excess is added. The *p*H should be about 8. The precipitate is digested for an hour on the steam bath, with the occasional addition of a few drops of dilute ammonia to replace that which evaporates. (The precipitate may be partially or completely redissolved if sufficient ammonia is not present during the digestion.) The solution is filtered through a medium or fine porosity filtering crucible[19] and the precipitate is washed with hot water. The filtrate should be tested for completeness of precipitation. The red complex is dried for 45 minutes at 110–120°C., cooled, and weighed. The salt, $NiC_8H_{14}O_4N_4$, contains 20.32% nickel.

Volumetric Determination.[20] Instead of weighing the nickel dimethylglyoxime complex, it may be titrated as follows: the compound is washed free of excess precipitant and dissolved in 15–20 ml. of warm diluted (1:2) sulfuric acid. The filter is washed thoroughly with hot 1% acid. Filtrate and washings are concentrated to about 25 ml. and 50 ml. of a ferric sulfate solution containing 40 g. per liter is added. The mixture is heated for 5 minutes, cooled, and diluted with 150 ml. of water containing 3 ml. of phosphoric acid (sp. gr. 1.7). The solution is titrated at once with 0.1 *N* permanganate. One ml. of 0.1000 *N* potassium permanganate is equivalent to 0.7335 mg. nickel.

Other Volumetric Methods. Among the volumetric methods for the analysis of dimethylglyoxime precipitates are the following: (*1*) the cyanometric titration of the nickel in the precipitate[21]; (*2*) bromate oxidation of the hydroxylamine liberated when the complex is decomposed in acid[22]; (*3*) solution of the complex in excess of standard acid, the excess being determined alkalimetrically,[23] and (*4*) dichromate oxidation of the nickel–dimethylglyoxime complex.[24] In the fourth

[19] Attention has been called to the fact that highly alkaline solutions may dissolve a sufficient amount of glass from the sintered disk to cause appreciable errors in the determination of small quantities of nickel. See V. Aleksandrov, *Zavodskaya Lab.*, **10**, 447 (1941); *Chem. Abstracts*, **38**, 4216 (1944).

[20] B. Tougarinoff, *Ann. soc. sci. Bruxelles*, **54B**, 314 (1934).

[21] I. I. Pomerantz, *Zavodskaya Lab.*, **4**, 966 (1935); *Chem. Abstracts*, **30**, 985 (1936).

[22] N. H. Furman and J. F. Flagg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 738 (1940).

[23] S. W. Parr and J .M. Lindgren, *Trans. Am. Brass Founder's Assoc.*, **5**, 120 (1912); *Chem. Abstracts*, **6**, 1579 (1912).

[24] S. Ishimaru, *J. Chem. Soc. Japan*, **54**, 367 (1933); *Chem. Abstracts*, **27**, 5025 (1933).

method an excess of dichromate in sulfuric acid is used to oxidize the complex. The excess may be determined with ferrous sulfate and permanganate, or probably by direct titration with ferrous sulfate using ferroin indicator. According to the author, 1 ml. 0.1000 *N* potassium dichromate is equivalent to 0.240 mg. nickel. This method seems to have definite possibilities in the determination of small amounts of nickel, and deserves further study.

2. Precipitation in Acetate Buffer

This procedure is required when considerable cobalt, manganese, or zinc is present.

The solution should contain a total of no more than 100 mg. of metals per 100 ml., and should be free from interfering elements of the hydrogen sulfide group. Elements precipitated by the basic acetate method should also be absent—removed, if necessary, by that method. If a basic acetate separation has been made, the filtrate from it is heated to boiling and the solution is adjusted to contain 1% acetic acid and 5% sodium acetate. An excess of dimethylglyoxime is added, and the determination is continued as described on page 147.

If the basic acetate separation was not necessary, the acidity is adjusted by neutralizing so that no more than 1 ml. hydrochloric (or sulfuric) acid is present per 200 ml. The solution is heated to boiling; dimethylglyoxime is added and then 20% sodium acetate solution until a precipitate appears. An excess of 10 ml. is added; the precipitate is digested for 30–45 minutes, and the determination is concluded as described on page 147.

A. Microdetermination of Nickel[25–27]

The weakly acidic solution of the nickel salt is treated in a filter beaker or microbeaker with excess dimethylglyoxime reagent. The solution is neutralized with ammonia, heated to 70°, cooled, and filtered. The precipitate is washed 5 or 6 times with 20% alcohol, and dried at 110°.

B. Determination of Nickel in Nonferrous Alloys

The large number of alloys in which nickel is a constituent precludes the possibility of giving detailed directions for the determina-

[25] I. Pollak, *Mikrochemie*, **2**, 17 (1924).
[26] R. Strebinger and J. Pollak, *ibid.*, **2**, 125 (1924).
[27] E. Kroupa, *Mikrochim. Acta*, **3**, 306 (1938).

tion of the element. However the main outlines of the various types of analyses required can be given, together with some specific illustrations.

It will be convenient to classify nonferrous alloys according to their nickel content. In one group, nickel is a major constituent. This group includes alloys such as German silver, Monel metal, coinage metals, and Nichrome. The other group, containing nickel as a minor constituent, includes brass and bronze, solders and soft metals, and the light alloys of aluminum, zinc, and magnesium. The alloys of the first group, with the exception of Nichrome, contain appreciable amounts of copper. This is usually removed by electrolysis in the course of a systematic analysis, and nickel may be determined easily in the residual solution. Any iron present is prevented from interfering by the addition of tartrate. The determination would be carried out as described on page 146. In the case of Nichrome, nickel is determined directly in the presence of the other constituents.

In Nichrome[23]

One gram of the alloy is weighed into a 600-ml. beaker and dissolved in 20 ml. nitro–hydrochloric acid (10 ml. nitric acid, sp. gr. 1.42; 30 ml. hydrochloric acid, sp. gr. 1.18; and 40 ml. of water). After adding 20 ml. sulfuric acid (1:1) the solution is evaporated to fumes. When cool, 100 ml. water is added and the solution is digested to dissolve salts. The solution is filtered; if a residue is present, it is washed with dilute (1:99) sulfuric acid. The residue is transferred to a platinum dish or crucible, dried, and ignited, and 2 ml. hydrofluoric acid and 2 drops sulfuric acid (sp. gr. 1.84) are added. The acids are evaporated; excess sulfuric acid is fumed off, and the residue is fused with a little sodium carbonate. The melt is dissolved in hydrochloric acid and added to the main solution.

The nickel solution is made up to 250.0 ml. in a volumetric flask. Into a 600-ml. beaker is pipetted a 50-ml. aliquot of the solution, 25 ml. 20% tartaric acid is added; the solution is made alkaline with ammonia and then acid with 15 ml. hydrochloric acid (sp. gr. 1.18) in excess. To the solution is added 20–30 ml. 3% sodium dimethylglyoxime, followed by ammonia to neutralize. The solution is made just acid with acetic acid, stirred, and allowed to stand at 75–90°C. 30 minutes. The precipitate is filtered on a filtering crucible, washed with

[23] *A. S. T. M. Methods of Chemical Analysis of Metals.* December 1936, p. 203.

hot water, and dried at 110°C. The complex $NiC_8H_{14}N_4O_4$ contains 20.32% nickel.

In the case of alloys containing nickel as a minor constituent, some of the principal elements are removed initially. Thus, in the analysis of brass and(or) bronze, tin, lead, and copper may be determined before the nickel. In the analysis of aluminum alloys, the residue insoluble in sodium hydroxide is examined for nickel,[29, 30] or tartrate (or citrate) is added and the determination is made directly in the presence of aluminum.[31, 32] German silver is conveniently analyzed for nickel using dimethylglyoxime,[33] as are copper alloys containing nickel and antimony.[34]

C. Determination of Nickel in Ferrous Materials

The specific precipitation of nickel in the presence of the unusually large number of foreign elements found in steel is one of the more spectacular accomplishments of organic reagents. Many methods have been published on the determination of nickel in steel.[35–50]

Only the A. S. T. M. methods[28] will be given here, since it is considered that these methods incorporate the best features of the many separate publications.

[29] M. D. Trykov and V. A. Lapskina, *Zavodskaya Lab.*, **10**, 253 (1941); *Chem. Abstracts*, **35**, 7314 (1941).
[30] M. L. Bertiaux, *Ann. chim. anal. chim. appl.*, **6**, 4 (1924); *Chem. Abstracts*, **18**, 953 (1924).
[31] H. A. Sloviter, *Ind. Eng. Chem., Anal. Ed.*, **13**, 235 (1941).
[32] J. Hanus and J. Sebor, *Chem. Listy*, **35**, 150 (1941); *Chem. Abstracts*, **37**, 3693 (1943).
[33] F. Ibbotson, *Chem. News*, **104**, 224 (1911).
[34] R. Woollen, *Foundry Trade J.*, **70**, 216 (1943); *Metal Ind. (London)*, **63**, 88 (1943).
[35] O. Brunck, *Stahl u. Eisen*, **28**, 231 (1908).
[36] H. Wdowiszewskii, *ibid.*, **28**, 960 (1908).
[37] A. Iwanicki, *ibid.*, **28**, 1546 (1908).
[38] P. Bogolubow, *ibid.*, **28**, 331 (1910).
[39] H. Schilling, *Chem. Ztg.*, **35**, 1190 (1911).
[40] H. König, *ibid.*, **37**, 1106 (1913).
[41] N. Welwart, *ibid.*, **37**, 1224 (1913).
[42] O. Bauer and E. Deiss, *ibid.*, **37**, 1374 (1913).
[43] P. Nicolardot and G. Gourmain, *Bull. soc. chim.*, **25**, 338 (1919).
[44] H. Rubricius, *Chem. Ztg.*, **46**, 26 (1922).
[45] H. Fettweis, *Stahl u. Eisen*, **45**, 1109 (1925).
[46] B. Jones, *Analyst*, **54**, 582 (1929).
[47] E. N. Deutschman, *J. Applied Chem. (U.S.S.R.)*, **8**, 1086 (1935).
[48] E. C. Pigott, *Ind. Chemist*, **11**, 273 (1935).
[49] G. Balz, *Z. anorg. Chem.*, **231**, 15 (1937).
[50] E. Reichel and L. Stuzin, *Z. anal. Chem.*, **113**, 389 (1938).

1. In Nickel Steels (0.05–3.5% Nickel)

Transfer 1 g. of the sample to a 400-ml. beaker, cover, and treat with 60 ml. diluted hydrochloric acid (1:1). (If less than 0.5% chromium is present, the sample may be dissolved in 50 ml. of hot nitric acid diluted 1:3.) Warm until decomposition is complete, and then cautiously add 10 ml. diluted nitric acid (1:1). Boil until iron and carbides are oxidized and oxides of nitrogen have been expelled. Dilute to 200 ml. with hot water. Add 20 ml. 25% tartaric acid solution, neutralize with ammonia, and add 1 ml. in excess. Filter any insoluble matter, and wash the paper and residue with hot water containing a little ammonia and ammonium chloride. Add hydrochloric acid until slightly acid, warm to 60–80°C., and add 20 ml. 1% dimethylglyoxime reagent. Add ammonia until slightly alkaline, and digest for 30 minutes at 60°C. (If the amount of nickel is small, or if much cobalt is present, the solution should be allowed to stand overnight at room temperature and filtered cold.)

If the steel contains less than 1% nickel, 2- or 3-g. samples may be used, taking correspondingly larger amounts of tartaric acid. For steels containing more than 3.5% nickel, a sample equivalent to about 35 mg. nickel is taken, or a suitable aliquot of a larger sample.

Filter the solution through a filtering crucible, but do not allow the mat to run dry. Wash the precipitate thoroughly with hot water. Add 5 ml. dimethylglyoxime reagent and 0.5 ml. ammonia to the filtrate and washings, stir, and allow to stand to determine whether precipitation is complete. Dry the precipitate at 150°C. to constant weight and weigh as $NiC_8H_{14}O_4N_4$, which contains 20.32% nickel.

If over 1% of cobalt, or 4% of copper, is present, a sufficient amount of reagent should be added to combine with them as well as the nickel, and the nickel should be reprecipitated as follows: when the precipitate has been washed, discontinue the suction, place the original beaker under the funnel, and add 25 ml. of a hot mixture of 20 ml. of diluted hydrochloric acid (1:1) and 5 ml. of nitric acid. After 1 minute apply suction until dry, and repeat the treatment with 25 ml. of acid mixture, drain, and wash thoroughly with 50 ml. of hot water containing 1 g. tartaric acid. Nearly neutralize the clear solution with ammonia and precipitate with dimethylglyoxime and ammonia as before.

2. In High-Nickel Steels (20% Nickel)

Transfer 0.35- to 0.5-g. of sample to a 400-ml. beaker and treat with 20 ml. diluted hydrochloric acid (1:1) and 20 ml. diluted nitric acid (1:1). Heat until solution ensues, add 20 ml. perchloric acid and evaporate just to light fumes (this step may be omitted for low-carbon, low-silicon alloys). Cool somewhat, and add 100 ml. water. Warm until salts dissolve, filter, and proceed as directed for nickel steels. Use 20–40 ml. of dimethylglyoxime reagent.

3. In Carbon Steels, Open-Hearth Iron, Wrought Iron, and Steels with Less Than 0.5% Nickel

Transfer 0.5 g. of sample to a 400-ml. beaker, and add 40 ml. diluted hydrochloric acid (1:1). Heat until solution is complete, and then carefully add 15 ml. diluted nitric acid (1:1). Evaporate to a volume of about 15 ml. and add 50 ml. diluted hydrochloric acid (sp. gr. 1.12). Transfer to a 200-ml. separatory funnel, rinsing the beaker with several 15-ml. portions of the diluted hydrochloric acid. Cool to 10°C., add 120 ml. ethyl ether, and carefully shake for 1–2 minutes in a stream of cold water. Let settle for several minutes and then draw off the lower clear solution into the original beaker. Gently heat the solution in the beaker to expel the ether, add 0.3 g. potassium chlorate, boil until the chlorate is decomposed, dilute to 100 ml., and add 3 g. tartaric acid. Make the solution alkaline with ammonia and filter. Acidify with hydrochloric acid and complete the determination as directed for nickel steels.

4. In Cast Irons

Dissolve 5 g. of the iron in 40 ml. diluted hydrochloric acid (1:1), carefully add about 15 ml. diluted nitric acid (1:1), and evaporate to dryness. Drench the hot dried mass with 10 ml. hydrochloric acid and then dilute with 75 ml. water. Filter, wash with diluted hydrochloric acid (1:1), and evaporate the filtrate to a syrupy consistency. Add 50 ml. hydrochloric acid (1:1), transfer to a 200 ml. separatory funnel, rinse the beaker with several small portions of the acid, add 120 ml. ether, and complete the determination as directed under *3* above.

5. In High-Nickel Chromium Alloy Cast Irons

Transfer a 2.5-g. sample to a 400-ml. beaker or flask and treat with a mixture of 25 ml. hydrochloric acid and 25 ml. nitric acid. When

solution is complete add 30 ml. perchloric acid, 5 to 10 drops hydrofluoric acid, and fume for 10 to 15 minutes after the chromium has been oxidized. Cool somewhat, add 100 ml. water and heat to boiling. Filter and wash well with diluted hydrochloric acid (5:95), catching the filtrate and washings in a 250 ml. volumetric flask. After making homogenous at 250 ml., 50-ml. aliquot portions are taken, and the analysis continued as described above for nickel steels.

D. Miscellaneous Determinations of Nickel

A method has been reported in which nickel is titrated with a standard solution of dimethylglyoxime, using dimethylglyoxime paper as a spot test indicator. The method is claimed to give good results in the presence of iron and aluminum hydroxides, silicic acid, and manganese dioxide.[51] Nickel may be titrated conductometrically with a standard solution of dimethylglyoxime, the accuracy being about one per cent.[52]

The "filtration method" (see page 161) has been applied in the determination of nickel with dimethylglyoxime[53]; also a method in which the hydrogen ion released when the nickel complex forms is determined alkalimetrically.[54]

Using dimethylglyoxime, nickel has been determined in ores,[55–59] meteoric iron,[60] and organic matter.[61]

E. Amperometric Titration of Nickel[4]

Nickel may be titrated amperometrically with a standard solution of dimethylglyoxime approximately 0.1 *M*, using the dropping mercury electrode as indicator electrode. The titration is carried out in a solution that is 0.5 *M* or less in ammonium chloride and about 0.5 *M* in ammonia at an applied potential of 1.85 v. on solutions ranging

[51] E. Block, G. Gad, and B. Krüger, *Metall. u. Erz.*, **37**, 495 (1940); **38**, 325 (1941); *Chem. Abstracts*, **35**, 3554 (1941); **36**, 5726 (1942). See also S. Sen, *J. Indian Chem. Soc.*, **21**, 311 (1945).

[52] J. H. Boulard, *J. Soc. Chem. Ind.*, **57**, 323T (1938).

[53] H. T. Bucherer and F. W. Meier, *Z. anal. Chem.*, **89**, 161 (1932).

[54] J. Holluta, *Monatsh.*, **40**, 281 (1919).

[55] O. Hackl, *Chem. Ztg.*, **46**, 385 (1922).

[56] H. F. Harwood and L. S. Theobald, *Analyst*, **58**, 673 (1933).

[57] J. G. Weeldenburg, *Chem. Weekblad*, **21**, 358 (1924).

[58] R. D. Midson, *Chem. Engineer Mining Rev.*, **29**, 196 (1937); *Brit. Chem. Abstracts*, **B**, 66 (1938).

[59] E. C. Krause, *Chemist-Analyst*, **30**, 6 (1941).

[60] E. P. Henderson, *Am. J. Sci.*, **239**, 372 (1941).

[61] H. W. Armit and A. Harden, *Proc. Roy. Soc. London*, **B77**, 420 (1906).

from 0.01 to 0.0001 *M* in nickel. The titration of 0.01 and 0.001 *M* solutions is accurate and precise to within 0.4%. With more dilute solutions an accuracy of 1 to 2% is obtained, and measurements should be made at points 20 to 40% removed from the end point to enable straight titration lines to be drawn.

Certain metallic ions, though not forming complexes with the reagent, may be reduced at the potential used but will not interfere seriously if their concentration is not much greater than that of the nickel. Iron is best removed by the basic benzoate method, while cobalt in excess of 5% of the nickel content of the solution should be removed prior to titration by means of precipitation as potassium cobaltinitrite.

III. Determination of Palladium

The use of dimethylglyoxime in the separation and determination of palladium ranks in importance with the use of that reagent in the determination of nickel. First proposed by Wunder and Thuringer[62] in 1912, the method has now practically superseded all others for the determination of palladium.

Precipitation of palladium(II) with dimethylglyoxime is quantitative in hydrochloric or sulfuric acid solution. Under the same conditions, gold is reduced by the reagent, and hence must be removed previously. This is usually done with hydroquinone or sulfur dioxide, both of which should be removed before proceeding with the palladium determination.[63] Platinum also interferes to various extents with the precipitation of palladium, depending on the conditions employed. It was originally recommended[62] that platinum be precipitated as ammonium chloroplatinate before determining palladium. Davis,[64] however, reported a satisfactory separation by precipitating palladium in the cold in the presence of platinum. Criticism of this method has been made,[65] although without a great deal of supporting data. Undoubtedly the best method for the separation of platinum and palladium (also rhodium and iridium) is that based on the hydrolytic precipitation of the latter elements in sodium bromate solution at *p*H 7.[66–68] Palladium may be separated by a single precipitation with di-

[62] M. Wunder and V. Thuringer, *Chem. Ztg.* (ii), 550 (1912); *Ann. chim. anal. chim. appl.*, **17**, 201, 328 (1912); *Z. anal. Chem.*, **52**, 101, 660, 740 (1913).
[63] F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 460 (1937).
[64] C. W. Davis, *Bur. Mines Reports of Investigations*, No. 2351 (1922).
[65] F. Krauss and H. Deneke, *Z. anal. Chem.*, **67**, 86 (1925).
[66] R. Gilchrist, *J. Research Natl. Bur. Standards*, **12**, 291 (1934).
[67] R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.* **57**, 2565 (1935).
[68] R. Gilchrist, *J. Research Natl. Bur. Standards*, **20**, 745 (1938).

methylglyoxime from rhodium and iridium, in either a chloride or sulfate solution.

Gold is precipitated quantitatively by dimethylglyoxime, while the precipitation of platinum by the reagent from hot solution is incomplete.[69] The platinum complex is $Pt(C_4H_7N_2O_2)_2$.[69, 70]

Palladium is determined as follows: to the solution containing no more than 100 mg. palladium in 250–300 ml., and acidified with 1 to 5 ml. hydrochloric acid (sp. gr. 1.18), is added an excess of dimethylglyoxime solution. The precipitate is allowed to stand for 1 hour, collected on a filtering crucible, and washed thoroughly with water. The complex is weighed after drying for 1 hour at 110°. $Pd(C_4H_7N_2O_2)_2$ contains 31.67% palladium.

Since the complex is not easily redissolved, the volumetric method is not applicable. An excess of standard dimethylglyoxime solution might be used, and the excess titrated, but there is no apparent advantage in this method.[20]

Methods have been described for the determination of palladium in dental alloys,[68, 71] in platinum,[72] and in bead assay work.[63, 73, 74] A separation of palladium and tin has been described.[75] A micromethod has been given by Holzer[76]; however, the fact that the precipitate must be ignited before final weighing detracts from the method. The palladium salt of methylbenzoylglyoxime may be dried and weighed, and hence should be used in microgravimetric determinations.[76]

A method for the determination of as little as 0.05% palladium in the presence of considerable amounts of nickel has been reported.[77]

[69] S. O. Thompson, F. E. Beamish, and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 420 (1937).
[70] R. A. Cooper, *J. Chem. Met. Mining Soc. S. Africa*, **25**, 296 (1924–5).
[71] W. H. Swanger, *Sci. Papers Bur. Standards*, No. 532 (1926).
[72] H. E. Zschiegner, *Ind. Eng. Chem.*, **17**, 294 (1925).
[73] F. E. Beamish and J. J. Russell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 141 (1936).
[74] E. E. Halls, *Ind. Chemist*, **13**, 431 (1937).
[75] A. Gutbier and C. Fellner, *Z. anal. Chem.*, **54**, 205 (1915).
[76] H. Holzer, *Z. anal. Chem.*, **95**, 392 (1933).
[77] Z. E. Gol'braĭkh, *J. Gen. Chem.* (*U.S.S.R.*,) **14**, 810 (1944); *Chem. Abstracts*, **39**, 3754 (1945).

CHAPTER XI

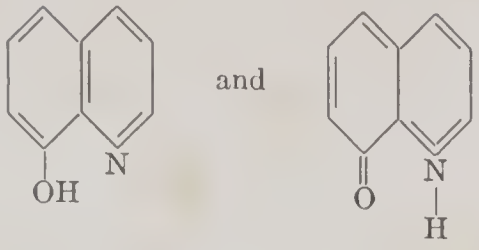
8-Hydroxyquinoline (Oxine)

Molecular weight: 145.15
Melting point: 74–76°C.
Solubility: soluble in acetone, alcohol, acetic acid, chloroform, etc.; slightly soluble in water
Reagent solutions: (*1*) 3% in methyl or ethyl alcohol (cannot be used for determining aluminum), or in acetone; should be protected from light. (*2*) 2 or 3% in acetic acid, prepared by dissolving the proper quantity of solid in glacial acetic acid and diluting to make the acid 1 or 2 *N*. Stable indefinitely in amber bottles. The alcohol solution may be employed in cases where precipitation occurs at a high *p*H; the acetic acid solution, for precipitations at low *p*H.

8-Hydroxyquinoline is one of the best known organic reagents, as well as being one of the most versatile; in excess of thirty elements may be determined or detected by methods involving the use of this compound. The literature pertaining to the use of 8-hydroxyquinoline is extensive, but is well summarized in numerous places.[1–3] Probably the widest use of the reagent has been in the determination of elements such as aluminum and magnesium, although methods have been devised for determining many others.

Pure 8-hydroxyquinoline (oxine) is an almost colorless solid, and gives colorless solutions in anhydrous organic solvents. Small amounts of water cause these solutions to assume a yellow color, presumably associated with an equilibrium involving the two forms given on the following page:

[1] R. Berg. *Das O-Oxychinolin*, Vol. 34 in series *Die Chemische Analyse*. 2nd Ed., Enke, Stuttgart, 1938.
[2] *Organic Reagents for Metals*. 4th Ed., Hopkin and Williams, London, 1943.
[3] J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*. Wiley, New York, 1941.



As might be deduced from inspection of the formula, oxine is an amphoteric electrolyte. Both acid and base functions are very weak, however; K_a is 2×10^{-10}* and K_b is 1×10^{-10}.[1] At 18°C. the isoelectric point is at *p*H 7.2, and at this *p*H the reagent shows the minimum solubility in water. This is of practical interest in that it indicates the conditions under which precipitation of the reagent itself is most likely to occur. Precipitation of the reagent is rather easily mistaken for precipitation of the organometallic complex.

Oxine reacts with metallic ions forming complex salts in which the metal is bound in a five-membered ring. The reagent functions as a monobasic acid; since it is a very weak acid, the formation of the insoluble complexes depends on the *p*H. This complex formation varies according to the solubility products of the oxinates, with the very insoluble copper oxinate being precipitated at low *p*H, while the calcium and magnesium complexes require quite strongly alkaline solutions to make their precipitation quantitative. Data on the *p*H effect in precipitations have been given by a number of workers, whose results are summarized in Chapter III (Table VII, page 52). Theoretical limitations in the use of these data are discussed at that point. A number of separations are possible, however, in cases where close control of *p*H is not required, as for example in the separation of metals whose oxinates are insoluble in distinctly acid solution (copper, cobalt, nickel, iron) from others, such as calcium and magnesium, that precipitate only at high *p*H. Inspection of Table VII (page 52) reveals other separations that might be feasible, *i.e.*, cadmium and tungstate, uranyl and cadmium, and uranyl and tungstate from molybdenum.[4]

In general, the entire matter of separations using oxine by means of controlled *p*H needs further study; particularly with respect to principles stated in Chapter III.

* A recent measurement by K. G. Stone and L. Friedman [*J. Am. Chem. Soc.*, **69**, 209 (1947)] gives 4.2×10^{-11} as the acid ionization constant.

[4] H. R. Fleck, *Analyst*, **62**, 378 (1937).

TABLE XX

Extraction of Hydroxyquinolates by Chloroform

Ion	*p*H Range for complete extraction of hydroxyquinolate
Aluminum	4.3 to 4.6
Bismuth	4.0 to 5.2
Cadmium	5.5 or higher
Cobalt	6.8 or higher
Copper(II)	2.7 to 7.0 (at least)
Iron(III)	1.9 to 3.0
Nickel	6.7 or higher
Zinc	5.5 or higher

Separations using oxine may also be effected by application of various complexing agents. Thus, iron and(or) titanium may be separated from aluminum by precipitation in an acetic acid solution containing malonic acid to form a complex with aluminum. Potassium cyanide may be used to prevent the precipitation of mercury, copper, and other metals by oxine, thus permitting separations to be made. In the presence of alkali tartrate, copper may be precipitated, while elements such as aluminum, antimony(V), arsenic(V), bismuth, chromium(III), iron(III), lead, and tin(IV) are not precipitated.

The fact that various metal oxinates are extracted from aqueous solution by chloroform at different *p*H values has been suggested by Moeller[5] as a means of separating the metals. His data, given in Table XX, indicate that it should be possible to separate iron from aluminum, cobalt, nickel, or bismuth, and copper from cobalt, cadmium, or zinc (and possibly from nickel and aluminum). Although the determinations described by Moeller were made spectrophotometrically on the extracted complexes, there is no reason to believe that these separations would not be useful preliminary steps in the course of gravimetric or volumetric analyses.

A few general conditions for conducting precipitations with oxine may be stated. (*1*) Precipitant is added to the cold solution until the yellow or orange-yellow color of the supernatant liquid indicates that a small but definite excess is present. (*2*) The precipitate is coagulated by a short period of heating at a temperature not exceeding 70°. Melting of the reagent (75°C.) should be avoided. Adherence of the

[5] T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 346 (1943).

precipitates to walls of vessels may be lessened by adding a trace of sodium taurocholate.[6] (*3*) Filtration may be made through paper or any variety of filtering crucible. (*4*) The filtrate should show a definite yellow or orange color, indicating the presence of excess precipitant. Should the filtrate become turbid upon standing, a portion should be reheated. If the turbidity disappears, it may be assumed to have been caused by excess precipitant, and is harmless. Otherwise, more reagent should be added, and the solution should be refiltered. (*5*) Hot or cold water is a satisfactory wash liquid for the oxinates, and is used until the filtrates becomes colorless. The last traces of oxine are difficult to wash out, however, particularly from bulky precipitates. The use of alcohol is permissible if it is known to be without effect on the precipitate. (*6*) Excess precipitant may be removed from the filtrate either by ether extraction of the alkaline solution or by evaporating the filtrate, meantime adding ammonia at frequent intervals. The second procedure is far superior to a nitric–sulfuric acid evaporation for removing excess oxine from a solution. After the precipitate has been formed, it can be treated in a number of ways.

A. Gravimetric Methods

(*1*) The complex is dried at 100–105°C. or at 130–140° and weighed. In cases where prolonged heating at 130–140° is required, decomposition may occur slowly. In general the weighing forms obtained at 100–105° are preferable. A table of weighing forms is given in the Appendix (page 283).

(*2*) The complex is ignited with oxalic acid (1–3 g.) and the metal is weighed as the oxide. Direct ignition of the complexes is undesirable because they are volatile.

B. Volumetric Methods

(*1*) Quantitative bromination of oxine with bromate–bromide reagent, a method developed by Berg, serves well for the volumetric determination of oxine precipitates. The general principles and technique have been described in Chapter V (page 87). The metal oxinate is dissolved in 50–100 ml. 2 *N* hydrochloric acid, and to the solution are added several drops of methyl red (0.2%) or indigo carmine (1%). Standard bromate–bromide reagent is then added slowly from a buret until the indicator turns yellow. A few milliliters excess of the

[6] C. G. Pope, *Biochem. J.*, 25, 1949 (1931).

bromate are added, followed immediately by 10 ml. 20% potassium iodide solution. The solution is titrated with 0.1 *N* (or weaker) sodium thiosulfate, preferably from a microburet. Starch is added near the end point. To aid in estimating the quantities of bromate reagent required, it should be noted that 1 millimole of a divalent metal will require 80 ml. of 0.1 *N* bromate, while 1 millimole of a trivalent metal will require 120 ml. of 0.1 *N* bromate. When comparatively large quantities of metal are involved, the use of 0.2 *N* bromate is desirable. In microdeterminations, 0.05 or 0.02 *N* bromate is used, and care is taken to establish the indicator blank. Copper and iron oxinates cannot be determined by this method, since both liberate iodine from potassium iodide. However, the presence of oxine does not interfere with the iodometric determination of copper and the precipitates may be analyzed for copper in this manner. Interference from iron can be prevented if phosphoric acid is added before the addition of the 10 ml. 20% potassium iodide in the above method.

(*2*) The "filtration method"[7] employs a standardized oxine–acetate solution, with which the unknown material is titrated. The equivalence point is reached when a portion of the solution being titrated gives, upon filtration, no reaction with the titrant. Phosphorus, magnesium, zinc, aluminum, and iron have been determined by this method. This method offers no advantage over the bromination method.

(*3*) The acidimetric method[8] makes use of the acid liberated when a cation is precipitated by oxine in a neutral solution. The amount of alkali needed to titrate the free hydrogen ion measures the amount of cation present.

$$M^{n+} + n\ C_9H_6NOH \rightarrow M(C_9H_6NO)_n + n\ H^+$$

(*4*) Wet oxidation with hexanitratocerate reagent offers promise for determinations on the micro scale[9, 10] (see Chapter V, page 89). Oxine, or the dissolved metal oxinate, is treated in 2 *M* perchloric acid with an excess of standard hexanitratocerate in 2 *M* perchloric acid. Oxidation is said to be complete in 15 minutes at 90–100°C. Upon cooling, the excess cerate is determined by titration with standard sodium oxalate, using Setopaline C as indicator (color change from red to yel-

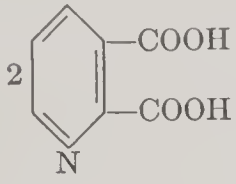
[7] H. T. Bucherer and F. W. Meier, *Z. anal. Chem.*, **82**, 10 (1930); **85**, 331 (1931).
[8] F. L. Hahn and E. Hartleb, *Z. anal. Chem.*, **71**, 225 (1927).
[9] J. P. Nielsen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 649 (1939).
[10] L. Gerber, R. I. Claassen and C. S. Boruff, *ibid.*, **14**, 658 (1942).

low). The cerate reagent is standardized with sodium oxalate using the same indicator. A blank determination must always be made. The oxidation consumes about 29.8 equivalents of cerate per mole of oxine, resulting in exceptionally favorable factors for elements such as aluminum. This same fact however limits the range of the method, and so far the applications have been with milligram quantities or less of magnesium. It should be noted too that the blank may be comparatively large when small samples are being determined.

Ceric sulfate has been found unsatisfactory for the oxidation of 8-hydroxyquinoline.[10]

(5) Wet oxidation with permanganate in acid solution has been reported.[11] In 2 *N* sulfuric acid at 80–90°C., the reaction is:

$$(C_9H_7ON)_2{\cdot}H_2SO_4 + 6\ KMnO_4 + 8\ H_2SO_4 \rightarrow$$



$$+ 3\ K_2SO_4 + 6\ MnSO_4 + 3\ CO_2 + HCO_2H + 10\ H_2O$$

The oxidation is apparently less complete than with cerate. The method is limited to the determination of not over about 2 mg. of magnesium, and it would seem that a further study of conditions is needed before it can be used with confidence.

In general, the volumetric methods are faster than the gravimetric especially when a series of determinations must be made. Added advantages are greater sensitivity, and the fact that the precipitate may be contaminated in certain cases—with silica, for example—without impairing the accuracy.

C. Microgasometric Method

This method, the principles of which have been discussed elsewhere (see pages 90 and 224), should find increasing use in the analysis of milligram quantities of oxine, or the oxinates. A method for the microdetermination of magnesium, based on the volume of carbon dioxide evolved when the magnesium complex is subjected to wet combustion, has been devised.[11a]

[11] L. D. Raskin, *Zavodskaya Lab.*, **5**, 1129 (1936); *Chem. Abstracts*, **31**, 968 (1937) See also *Chem. Abstracts*, **30**, 7486 (1936).

[11a] C. L. Hoagland, *J. Biol. Chem.*, **136**, 543 (1940).

I. Recommended Specifications for 8-Hydroxyquinoline[12]

A. Requirements

Melting point range: 72.5° to 73.5°C.
Insoluble in alcohol: not more than 0.050%
Residue on ignition: not more than 0.50%
Sulfate (SO_4): to pass test (limit about 0.02%)
Suitability for magnesium determination: to pass test

B. Tests

Melting Point Range. Determine by the U. S. Pharmacopoeia method.

Insoluble in Alcohol. Dissolve 3 g. in 40 ml. alcohol; filter through a Gooch crucible; wash with 95% alcohol; dry at 105–110°C., and weigh. The weight of the insoluble material should not exceed 0.0015 g.

Residue on Ignition. Ignite 1 g. The weight of the residue should not exceed 0.0005 g.

Sulfate. Dissolve 1 g. in 1 ml. hydrochloric acid and dilute with 20 ml. water. Heat to boiling and add 1 ml. barium chloride solution (10%). No turbidity should be observed after solution has been standing for 30 minutes.

Suitability for Magnesium Determinations. Dissolve 0.5 g. of magnesium chloride ($MgCl_2.6H_2O$) in water containing 1 ml. dilute hydrochloric acid (1:1) and make up to a volume of 100 ml. Dilute 10 ml. of the solution to 50 ml. and add 3.5 ml. of a solution of the 8-hydroxyquinoline prepared by dissolving 2.5 g. in 5 ml. warm acetic acid and pouring into 95 ml. water at 60°C. Heat to 80°C.; add with stirring 2 ml. ammonium hydroxide; allow to cool for 10 minutes, and filter. The filtrate should be yellow and alkaline, and should yield a yellow precipitate when 5 ml. of the magnesium chloride solution is added and the whole is warmed.

II. Determination of Aluminum

1. Precipitation in Acetic Acid–Ammonium Acetate Solution

Under these conditions aluminum is separated from the alkali metals, and from the alkaline earths including beryllium.[13, 14] All

[12] Committee on Analytical Reagents, *Ind. Eng. Chem., Anal. Ed.*, **12**, 631 (1940).
[13] I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928).
[14] G. E. F. Lundell and H. B. Knowles, *J. Research Natl. Bur. Standards*, **3**, 91 (1929).

other elements presumably interfere. If large quantities of aluminum are to be separated from small quantities of magnesium, this element should be first precipitated as hydroxide from an alkaline tartrate solution, and aluminum should be determined in the filtrate (see section on precipitation in ammoniacal tartrate below).

H. B. Knowles[15] has made a critical study of the precipitation of aluminum in acetic acid–acetate solution, and finds that with more than 50 mg. aluminum the results are high, probably because of occluded precipitant. He recommends working with 50 mg. or less for the gravimetric method, and 25 mg. or less for the volumetric method.

Chirnside, Pritchard, and Rooksby[16] examined the aluminum hydroxyquinolate by x-ray diffraction, and found it anhydrous and suitable for weighing after being dried at 98°C. The solution to be analyzed should contain no more than 50 mg. aluminum in a volume of 100 to 150 ml. A small amount of mineral acid may be present. The solution is heated to about 60°, and an excess of a 2% solution of oxine in acetic acid is added. Normally the excess amounts to 10–20% but when the quantity of aluminum is small, as much as 50% excess may be used. A solution of 2 *N* ammonium acetate is then added slowly until a permanent precipitate forms, followed by an excess of about 25 ml. The *p*H should be about 6.8[14] (brom cresol purple color change). The solution is allowed to cool, collected on a filtering crucible of fine porosity, and washed with cold water until the filtrate is colorless. The precipitate is dried at 120–140°, cooled, and weighed as $Al(C_9H_6ON)_3$ which contains 5.87% aluminum, or 11.10% Al_2O_3.

The determination may be concluded volumetrically. The precipitate is dissolved in the minimum quantity of (1:1) ethyl alcohol and 6 *N* hydrochloric acid, the solution is diluted to about 100 ml., and titrated as described on page 160. 1 ml. of 0.2 *N* potassium bromate is equivalent to 0.4495 mg of aluminum.

A volumetric cerate method has also been described.[16a]

2. Precipitation in Ammoniacal Tartrate Solution

The solution to be analyzed should contain no more than 50 mg. aluminum in 100 ml. Sufficient tartaric acid is added to prevent precipitation of aluminum hydroxide, followed by 2 g. of ammonium

[15] H. B. Knowles, *J. Research Natl. Bur. Standards*, **15**, 87 (1935).
[16] R. C. Chirnside, C. F. Pritchard, and H. P. Rooksby, *Analyst*, **66**, 399 (1941).
[16a] J. P. Mehlig, and C. J. Dernbach, *Chemist-Analyst*, **32**, 80 (1943).

chloride and ammonia to make the solution neutral. After heating to 60–70°, the aluminum is precipitated by dropwise addition of oxine in acetic acid. A small excess is used, followed by several drops of ammonia. Heating is continued for five minutes, the solution is allowed to stand until cool, and the precipitate is filtered, washed, dried at 120–140°, and weighed as $Al(C_9H_6ON)_3$, containing 5.87% aluminum, or 11.10% Al_2O_3. The determination may be concluded volumetrically as described above.

A. Microdetermination of Aluminum[17]

One milliliter of solution, containing 0.05 to 0.025 mg. of aluminum, is treated with a drop of hydrochloric acid and 0.5 ml. of oxine reagent (in acetic acid). After being heated to 60°C., 2 *N* ammonium acetate is added dropwise until a turbidity appears; after 1 minute, 0.5 ml. more is added. After standing at 60° for 10 minutes the precipitate is collected on a filter stick, washed with 0.25 to 0.5 ml. of hot water, dried for 5 minutes at 140°, and weighed as $Al(C_9H_6ON)_3$.

B. Separation of Aluminum from Other Elements

1. From Iron[18, 19]

The solution containing aluminum and iron is treated with tartaric acid sufficient to form a complex with the aluminum, and then is made alkaline with ammonia. Sufficient potassium cyanide is added to form the ferricyanide complex; the solution is heated to boiling, and sodium sulfite (or hydroxylamine hydrochloride) is added to reduce the ferricyanide. Aluminum is then determined as outlined on page 164.

2. From Uranium[14]

The acetic acid solution containing aluminum and uranyl ions (maximum of 50 mg. of UO_2^{++}) is treated with an excess of oxine reagent, and neutralized with saturated ammonium carbonate solution. After 3–6 g. solid ammonium carbonate is added, the solution is diluted to 150 ml. and heated to about 90°C. until the uranyl hydroxyquinolate has dissolved, and only the greenish-yellow aluminum hydroxyquinolate remains. The precipitate is filtered, washed, and dissolved in a minimum amount of hydrochloric acid. This solution is

[17] A. Benedetti-Pichler, *Mikrochemie*, Pregl-Festschrift, (1929).
[18] R. Lang and J. Reifer, *Z. anal. Chem.*, **93**, 161 (1933).
[19] Modified by R. Berg; see reference 1, p. 52.

neutralized with ammonia, acidified slightly with acetic acid, and the aluminum is reprecipitated as above. The complex is dried, and weighed as usual, or titrated (see page 160).

3. From Columbium, Molybdenum, Tantalum, Titanium, and Vanadium[14]

The solution is prepared as described on page 164. Immediately before addition of the oxine, 15 ml. 3% hydrogen peroxide is added per 100 ml. total volume. The rest of the procedure is as described on page 164.

4. From Phosphate

(*a*)[14] The mineral acid solution (which may also contain arsenic or boron) containing no more than 50 mg. aluminum in 100 ml. is treated with an excess of oxine, neutralized with ammonia, and, after being heated to 60–70°C., treated with an excess of 5 ml. 2 *N* ammonia. When cool, the precipitate is collected on paper and washed with a cold solution of (1:40) ammonia containing 25 ml. of the oxine reagent per liter. Precipitate and paper are fumed with sulfuric acid, and a few milliliters of nitric acid are added to the solution. When organic matter is destroyed, the solution is cooled, and perchloric acid (60–70%) equal to one-third the volume of the solution is added. Heating is required to make the solution colorless; it is then cooled, diluted, and treated with ammonia to precipitate the aluminum. The aluminum hydroxide is filtered, washed, and ignited. It is possible that the aluminum hydroxyquinolate could be washed with cold water, dried, and weighed in the usual manner.

(*b*)[20, 21] Amounts of aluminum ranging from 2 to 50 mg. may be precipitated in the presence of 10 mg. phosphorus pentoxide from ammoniacal tartrate solution. The method follows that given on page 164.

(*c*)[22, 23] In the presence of as much as 200 mg. phosphorus pentoxide, from 2 to 15 mg. aluminum may be determined as follows. The solution, 30 ml. in volume, is treated with 0.2 *N* sodium hydroxide until the aluminum phosphate redissolves, or until a phenolphthalein color change is observed. An excess of base should be avoided. The solution is diluted to 100 ml., heated to 45–50°C., and precipitated with excess

[20] R. Berg, quoted in reference 1, page 55.
[21] E. Jung, *Z. Pflanzenernähr. Düngung u. Bodenk.*, **A26**, 1 (1932).
[22] G. Balanescu and M. D. Motzoc, *Z. anal. Chem.*, **91**, 188 (1933).
[23] E. S. von Bergkampf, *ibid.*, **83**, 345 (1931).

4% alcoholic oxine. After it has been heated to boiling and kept hot for 5–10 minutes, the solution is allowed to cool to 50°; the precipitate is filtered, dried, and weighed (or titrated) as usual. The accuracy is said to be about 0.7%.

C. Determination of Aluminum in Complex Materials

A very large number of methods have been given for determining aluminum in complex materials with the aid of oxine. Naturally, details of all such methods cannot be given. In most cases the principal problem is one of separating the aluminum from interfering ions, and obtaining it in solution suitable for precipitation by oxine. A few typical cases, representing a variety of materials, will be given.

1. In Feldspar[15]

In this simple case, the interfering elements, *e.g.*, iron, titanium, and zirconium, are present in such small amounts as to cause no error in ordinary analyses. The sample should represent 0.1 g. of feldspar. It may be the filtrate from the silica determination, or a sample from which silica has been removed by sulfuric–hydrofluoric acid treatment. (Complete removal of fluoride is essential.) Aluminum is precipitated from the solution by the method described on page 163.

Other methods for determining aluminum in siliceous materials are found in the literature as follows: silicates and clays,[24–34] glasses,[35] and cement.[36]

2. In Nitriding Steel[37]

Four grams of sample is heated with 50 ml. sulfuric acid (1:9) until

[24] J. Robitschek, *Sprechsaal*, **61**, 233 (1928).
[25] J. Robitschek, *J. Am. Ceram. Soc.*, **11**, 587 (1928).
[26] G. Krinke, *Sprechsaal*, **64**, 556 (1931).
[27] S. S. Shukovskaya and S. T. Baljuk, *Zavodskaya Lab.*, **3**, 485 (1934); *Brit. Chem. Abstracts*, **B**, 834 (1934).
[28] F. Klasse, *Ber. deut. keram. Ges.*, **15**, 560 (1934); **16**, 628 (1935).
[29] S. S. Shukovskaya and M. I. Volinetz, *Zavodskaya Lab.*, **3**, 616 (1934); *Brit. Chem. Abstracts*, **B**, 1009 (1934).
[30] H. B. Knowles and J. C. Redmond, *J. Am. Ceram. Soc.*, **18**, 106 (1935).
[31] W. Steger, *Ber. deut. keram. Ges.*, **16**, 624 (1935).
[32] K. Schoklitsch, *Mikrochemie*, **20**, 247 (1936).
[33] P. Urech, *Z. anal. Chem.*, **111**, 337 (1938).
[34] E. W. Koenig, *Ind. Eng. Chem., Anal. Ed.*, **11**, 532 (1939).
[35] R. C. Chirnside, *J. Soc. Glass Tech.*, **19**, 279 (1935).
[36] L. Kampf, *Ind. Eng. Chem., Anal. Ed.*, **13**, 72 (1941).
[37] H. A. Bright and R. M. Fowler, *J. Research Natl. Bur. Standards*, **10**, 327 (1933).

action ceases. The solution is diluted to 150 ml. with hot water, boiled, and treated with sodium bicarbonate solution (8 g. per 100 ml.) from a buret until a white precipitate forms. An excess of 0.2 ml. for each milligram of aluminum anticipated, or 5 ml., whichever is greater, is added. The reaction flask is covered, the contents are boiled for 1 minute, and the precipitate is allowed to settle. The precipitate is collected on Whatman No. 40 (or equivalent) paper, and flask and precipitate are washed twice with hot water.

The bicarbonate precipitate is dissolved off the paper with 25 ml. hydrochloric acid (1:2), and the solution is collected in the reaction flask. Filter and residue are washed 8 to 10 times with hot hydrochloric acid (1:19), and the washings are collected in the same flask. To the combined acid solution and washings is added 1 ml. nitric acid (sp. gr. 1.42). The solution is boiled for 2 minutes, then cooled. Thirty per cent sodium hydroxide is added until the solution is nearly neutral; the volume is adjusted to 150–175 ml. and the solution heated to 70°C. and poured with stirring into 150 ml. hot 10% sodium hydroxide. After it has been boiled for 1 minute, the solution is allowed to cool to room temperature, and is then made up to 500 ml. in a volumetric flask. The entire amount is poured into a dry 600-ml. beaker, stirred, and allowed to settle for 30 minutes. The solution is filtered through Whatman No. 42 paper; the first 25–30 ml. is discarded and the next 250 ml. is collected in a volumetric flask.

The 250 ml. is transferred quantitatively to a 600-ml. beaker and neutralized with hydrochloric acid, adding 3–5 ml. acid (sp. gr. 1.18) in excess. One gram of tartaric acid is added, then ammonia (sp. gr. 0.90) to make the solution alkaline to litmus, plus an additional 3–4 drops. Ten to fifteen milliliters of 3% hydrogen peroxide is added and the determination is concluded as outlined on pages 164 and 165.

Other methods for determining aluminum in ferrous materials have been described. These methods employ oxine as the final precipitant for aluminum, and use conventional means such as hydrogen sulfide precipitation, electrolysis with a mercury cathode, etc., for bulk separation of impurities. Included are means for determining aluminum in: ferrovanadium and ingot iron,[38–40] steel,[41–45b] slags and ores,[46] and cast iron.[47]

[38] J. Haslam, *Analyst*, **58**, 270 (1933).
[39] S. L. Tzinberg, *Zavodskaya Lab.*, **3**, 1129 (1934); *Brit. Chem. Abstracts*, **B**, 410 (1935).
[40] Z. S. Muchina, *Zavodskaya Lab.*, **5**, 715 (1936); *Brit. Chem. Abstracts*, **B**, 563 (1937).

Two general methods are applicable—the choice depends somewhat on the nature of the sample. (*a*) The method of Hezcko[48] allows aluminum to be precipitated directly in the presence of chromium, cobalt, copper, iron, manganese, molybdenum, and nickel. Potassium cyanide and tartaric acid are used to retain interfering ions in solution. This method has been adapted by Reutel[49] to the analysis of zinc and zirconium alloys. (*b*) Preliminary separation of aluminum as hydroxide[50] or basic benzoate[51] is used when zinc and magnesium are major constituents of the alloy.

(*a*) Reutel's method, in which iron, copper, molybdenum, nickel, chromium, and zinc are said not to interfere, is as follows: A 0.2-g. sample is dissolved in a little 7.5 *N* nitric acid; 3–4 g. citric acid is added, followed by 1–2 g. ammonium chloride and sufficient ammonia to make the solution basic. One gram of sodium sulfite is added; the solution is heated to boiling, and 6–7 g. potassium cyanide is added. Aluminum is precipitated by dropwise addition of 8 ml. 5% alcoholic oxine. The determination is concluded volumetrically (see page 160).

(*b*) The benzoate method of Stenger *et al.* is as follows: The sample should be chosen to contain from 0.2 to 0.5 g. aluminum. It is placed in a 250-ml. beaker with 25 ml. of water and dissolved by adding in small portions a total of 10 ml. hydrochloric acid for each gram of sample. When action is complete the solution is cooled and diluted to 500 ml. in a volumetric flask. Any copper or carbon residue may be allowed to settle, but silica should be kept suspended in the solution. A 50-ml. aliquot is pipetted into a 400-ml. beaker and diluted with 50 ml. water.

To the solution is added ammonium hydroxide (1:1) dropwise until the free acid is almost completely neutralized. Then 1 ml. glacial

[41] A. Dimov and R. S. Moltschanova, *Zavodskaya Lab.*, **5**, 718 (1936); *Brit. Chem. Abstracts*, **B**, 563 (1937).
[42] P. Klinger, *Arch. Eisenhüttenw.*, **13**, 21 (1939).
[43] E. C. Pigott, *J. Soc. Chem. Ind.*, **58**, 139 (1939).
[44] G. E. Speight, *J. Iron Steel Inst., London*, Section VIII, 77 (1941); *Chem. Abstracts*, **35**, 4705 (1941).
[45] E. C. Pigott, *Iron and Steel*, **16**, 325 (1943).
[45a] R. Stumper, *Chem. Ztg.*, **65**, 239 (1941).
[45b] S. D. Steele and L. Russell, *Iron and Steel, London*, **16**, 182 (1942).
[46] S. Y. Fainberg and E. M. Tel, *Zavodskaya Lab.*, **5**, 1307 (1936); *Chem. Abstracts*, **31**, 2118 (1937).
[47] E. Taylor-Austin, *Analyst*, **63**, 566 (1938).
[48] T. Heczko, *Chem. Ztg.*, **58**, 1032 (1934).
[49] C. Reutel, *Metall. u. Erz.* **38**, 170 (1941); *Chem. Abstracts*, **35**, 5819 (1941).
[50] C. H. Wood, *J. Soc. Chem. Ind.*, **61**, 29 (1942).
[51] V. A. Stenger, W. R. Kramer, and A. W. Beshgetoor, *Ind. Eng. Chem., Anal. Ed.*, **14**, 797 (1942).

acetic acid, 1 g. ammonium chloride, and 20 ml. ammonium benzoate solution (100 g. ammonium benzoate per liter, plus 1 mg. thymol as preservative) are added. The solution is then boiled for five minutes, with stirring, and filtered on a fine porosity filtering crucible which was weighed previously. The precipitate is washed 8 to 10 times with hot benzoate wash solution (100 ml. ammonium benzoate solution, 900 ml. water, 20 ml. glacial acetic acid), making no effort to transfer all the precipitate to the crucible.

The precipitate is returned to the beaker by means of a stirring rod and a jet of water. The crucible is washed out with five 10-ml. portions of hot ammoniacal tartrate solution (120 ml. ammonium hydroxide, sp. gr. 0.90; 30 g. ammonium tartrate; water to make 1 liter) which are combined with the precipitate in the beaker. After the contents of the beaker are heated to about 70°C., 25 ml. oxine is added, and the precipitate is digested for 30 minutes. The precipitate is filtered on the original crucible, washed eight times with water, dried, and weighed as usual.

(*c*) Other methods have also been reported for determining aluminum in alloys.[52–53a]

D. Amperometric Titration of Aluminum

Aluminum, copper, and zinc are reported[54] to have been determined amperometrically by titration with oxine in buffered acetate solutions. Details are lacking.

E. Miscellaneous Determinations of Aluminum

Methods have been described for determining aluminum in foods,[55] aluminum protein compounds,[56] plant ash,[57] sea water,[58] and titanium pigments.[58a] In these, as in the other methods, the use of oxine is advantageous because of the ease with which the aluminum may be precipitated and the variety of ways in which the determination may be concluded.

[52] E. E. Halls, *Ind. Chemist*, **17**, 120 (1941); *Chem. Abstracts*, **36**, 3119 (1942).
[53] A. T. Etheridge, *Analyst*, **67**, 9 (1942).
[53a] F.F. Pollack and E. F. Pellows, *J. Chem. Soc.*, **1945**, 300.
[54] A. M. Zanko, *Dopovidi Akad. Nauk U.S.S.R.*, **1940**, **27**, 32; *Chem. Zentr.* **1942**, II, 1606; *Chem. Abstracts*, **37**, 5921 (1943).
[55] K. B. Lehmann, *Arch. Hyg. Bakt.*, **106**, 309 (1931).
[56] C. G. Pope, *Biochem. J.*, **25**, 1949 (1931).
[57] L. Hart, *J. Assoc. Off. Agric. Chem.*, **15**, 285 (1932).
[58] H. M. Haendler and T. G. Thompson, *J. Marine Research*, **2**, 12 (1939).
[58a] I. Baker and G. Martin, *Ind. Eng. Chem., Anal. Ed.*, **17**, 488 (1945).

III. Determination of Cadmium

Cadmium may be precipitated by oxine either from an acetic acid solution of *p*H 5.4 or higher or an alkaline tartrate solution[59] as $Cd(C_9H_6ON)_2 \cdot 2\,H_2O$, dried at 130°C., and weighed as $Cd(C_9H_6ON)_2$. By use of the first method, cadmium may be separated from alkaline earths and alkali metals, and, in the presence of potassium cyanide, from mercury; the second method affords a separation from aluminum, antimony(V), arsenic(V), bismuth, chromium(III), iron(III), lead, and tin.

1. Precipitation in Acetate Solution

The neutral or weakly acidic solution containing cadmium is treated with sodium carbonate until a turbidity appears, and then with sufficient acetic acid to just clear the solution. After the solution is heated to 60°, an excess of alcoholic oxine is added; the solution is boiled for a short time and allowed to cool to room temperature. The precipitate is filtered on a medium or fine filtering crucible, washed first with hot, then cold, water, and dried at 130°. The precipitate of $Cd(C_9H_6ON)_2$ contains 28.05% cadmium. Alternatively the precipitate may be dissolved in hydrochloric acid and titrated with bromate-bromide solution (p. 160). One milliliter of 0.1 *N* bromate corresponds to 1.405 mg. cadmium. In the presence of mercury, 20 ml. 0.5 *N* potassium cyanide should be added before neutralizing with sodium carbonate.

2. Precipitation in Tartrate Solution

To the solution is added 2–5 g. tartaric acid per 100 ml., followed by sufficient 8–10 *N* sodium hydroxide to neutralize the solution to phenolphthalein. An excess of 10–12 ml. 2 *N* base is added per 100 ml. total volume. The cadmium is precipitated in the cold with 3% alcoholic oxine. Several minutes may elapse before precipitation begins. The solution is heated to 60°C., stirred until the precipitate becomes crystalline, and collected on a filtering crucible. The determination is concluded as described above for the acetate precipitation. If the impurities total more than 200 mg., reprecipitation is necessary.

A. Microdetermination of Cadmium[60]

The determination is carried out using a filter beaker, or a microbeaker and filter stick. To the neutral or weakly acidic solution, con-

[59] R. Berg, *Z. anal. Chem.*, **71**, 321 (1927).
[60] P. Wenger, C. Cimerman, and M. Wyszewianska, *Mikrochemie*, **18**, 182 (1935).

taining no more than 3 mg. cadmium in a volume of about 2 ml., is added 1 drop of universal indicator followed by 1 drop 3% sodium carbonate solution. Any turbidity or precipitate is then eliminated by adding 2 or 3 drops 3% acetic acid. The *p*H is brought to 6–7 by dropwise addition of 40% sodium acetate solution. The mixture is heated to 80–90°C. and a three fold excess of 2% oxine in alcohol is added dropwise. The mixture is shaken while heating is continued almost to the boiling point. The precipitate is filtered after standing for 15–20 minutes, and then washed, first with two 1-ml. portions of hot water, then with the same amount of cold water. The precipitate is dried at 130° and weighed as $Cd(C_9H_6ON)_2$ which contains 28.05% cadmium.

IV. Determination of Copper

In common with other reagents (quinaldic acid, anthranilic acid, salicylaldoxime), oxine precipitates copper quantitatively from moderately acidic solutions, effecting its separation from the alkaline earths, alkali metals, and many common cations. It may also be used to precipitate copper from ammoniacal tartrate solutions, whereby that element is separated from aluminum, antimony(V), arsenic(V), bismuth, chromium(III), iron(III), lead, and tin(IV). The insoluble complex, $Cu(C_9H_6ON)_2$, is readily dried at 105–110°C.

1. Precipitation in Acid Solution[48, 61–63]

To the neutral or slightly acidic solution containing not over 100 mg. copper in 100–150 ml. is added 3 g. ammonium acetate and 10 ml. glacial acetic acid. The solution is heated to 60°C. and the copper is precipitated by dropwise addition of 3% alcoholic oxine. A slight excess should be added. After it is heated briefly to 80–90°C., the precipitate is filtered, washed with hot water, and dried at 105–110°C. The precipitate of $Cu(C_9H_6ON)_2$ contains 18.08% copper. The filtrate may be analyzed for other ions (magnesium, cadmium, etc.) which may have been present initially, and were not precipitated by the oxine.

2. Precipitation in Alkaline Tartrate Solution

This serves only for a preliminary separation of copper from interfering elements. The acid solution, containing from 3 to 100 mg. cop-

[61] R. Berg, *Z. anal. Chem.*, **70**, 341 (1927).
[62] M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan.* **55**, 1065 (1934).
[63] I. R. Shik, *Zavodskaya Lab.*, **9**, 1322 (1940); *Chem. Abstracts*, **35**, 2810 (1941).

per in the presence of not more than 50 mg. each of the interfering elements listed above, is treated with 3–5 g. tartaric acid, neutralized to phenolphthalein with strong sodium hydroxide, and, after 20 ml. 0.2 *N* base in excess is added, made up to 100 ml. Copper is precipitated from the cold solution by adding 3% alcoholic oxine. The precipitate is filtered after the solution is heated to 60–70°C. and cooled. The precipitate is washed with warm 1% sodium tartrate solution, dissolved in 2 *N* hydrochloric acid, and the copper is determined iodometrically. There are reports in the literature for the determination of copper in aluminum alloys[64] and in the presence of aluminum, bismuth, cadmium, cobalt, iron, lead, magnesium, manganese, molybdenum, nickel, silver, titanium, vanadium, and zinc.[65] Somewhat more thorough investigations of these methods seem warranted.[66] Zanko[54] has described the amperometric titration of copper with oxine.

V. Determination of Magnesium

Magnesium is precipitated by oxine at high *p*H as the yellowish-green complex $Mg(C_9H_6ON)_2 \cdot 4\,H_2O$. In buffered ammonia solution, magnesium may be separated under proper conditions from alkaline earths and alkali metals. Precipitation may also be made from an alkaline tartrate solution, under which conditions only copper, zinc, and cadmium precipitate with the magnesium.

Since the oxine method is potentially a very useful method for determining magnesium, particularly because the volumetric determination offers great advantages in speed, the general subject of magnesium determination by this method has been studied rather extensively. A review article on the determination has been published.[67]

Redmond and Bright,[68] in a study of the determination of magnesium in Portland cement and related substances, found that best results were obtained with the volumetric method if oxine was added to a hot solution containing ammonium salts and some ammonia, and if more ammonia was then added and the solution stirred vigorously (see page 85). An alternative method, which consisted of adding ammonia to the acid or neutral solution containing magnesium and

[64] J. Calvet, *Compt. rend.*, **195**, 148 (1932).
[65] S. L. Tzinberg, *Zavodskaya Lab.*, **4**, 1161 (1935).
[66] Reference 1, page 27.
[67] D. C. Vucetich, *Rev. facultad cienc. quim. Univ. nacl. La Plata*, **9**, 81 (1934); *Chem. Abstracts*, **36**, 6108 (1942).
[68] J. C. Redmond and H. A. Bright, *J. Research Natl. Bur. Standards*, **6**, 113 (1931).

oxine, gave low results—supposedly because of slow precipitation. These authors strongly recommend the volumetric method for concluding the determination.

In a critical study of the precipitation of magnesium by oxine, particularly with reference to silicate and carbonate rock analysis, Miller and McLennan[69] found that for best results the magnesium complex should be precipitated by adding oxine to an ammoniacal solution containing magnesium. The presence of a large excess of ammonium salts, or ammonia, has no important influence on the results. The amount of excess oxine, if not over 50%, is apparently of no importance, although with 100% excess the results with the volumetric method are high. For gravimetric determination, precipitates that are suspected to contain coprecipitated oxine should be dried at 160°; otherwise, drying as the dihydrate at 105° for one hour or longer is recommended. Good evidence[16] exists that the precipitate is anhydrous at 160°C.

The possibility of separating magnesium from metals precipitated by oxine at a lower *p*H also exists. Thus nickel and magnesium may be separated,[4] as may zinc and magnesium.[70] When aluminum is present in a small amount, it may be separated from magnesium by precipitation in acetic acid–acetate solution.[71] Small quantities of iron may be removed from the magnesium complex by dissolving the iron complex in chloroform, in which the magnesium complex is insoluble.[72] Since the magnesium hydroxyquinolate is less soluble than the magnesium phosphates, oxine affords a good method for separating magnesium from phosphate.[73, 74]

1. Precipitation in Buffered Ammonia Solution[68, 69, 75]

The magnesium solution should contain about 30 mg. or less magnesium in 100 ml., together with 2 g. ammonium chloride or acetate to prevent precipitation of magnesium hydroxide; 6 *N* ammonia is added to bring the *p*H up to 9.5 to 10, then a few milliliters in excess. A trace of sodium taurocholate should be added to prevent the precipitate from adhering to the beaker. The solution is heated to 80°C. and, depending on whether the amount of magnesium is large or small,

[69] C. C. Miller and I. C. McLennan, *J. Chem. Soc.*, **1940**, 656.
[70] H. V. Moyer and W. J. Remington, *Ind. Eng. Chem., Anal. Ed.*, **10**, 212 (1938).
[71] R. Berg, *Z. anal. Chem.*, **71**, 369 (1927).
[72] M. Arnoux, *Compt. rend. soc. biol.*, **116**, 436 (1934).
[73] S. Ishimaru, *J. Chem. Soc. Japan*, **55**, 732 (1934); **56**, 62 (1935).
[74] Reference 1, page 34.
[75] R. Berg, *Z. anal. Chem.*, **71**, 23 (1927).

5% or 1% oxine in 2 or 0.4 *N* acetic acid is added very slowly, with stirring, until a small excess is present, as shown by the deep yellow color of the supernatant liquid. A large excess of precipitant should be avoided, as there is danger that the reagent itself may precipitate.

The precipitate is digested for ten minutes on the steam bath, and is then collected on a filtering crucible of fine or medium porosity, washed with hot, 1% ammonia, and dried at 105° or 160°, for one hour, then for single half-hour periods. The complex obtained at 105°, $Mg(C_9H_6ON)_2 \cdot 2\,H_2O$, contains 6.98% magnesium; at the higher temperature $Mg(C_9H_6ON)_2$, containing 7.78% magnesium is produced.

Volumetric Methods. The precipitate may be dissolved in hydrochloric acid and determined volumetrically with potassium bromate. The precipitate is dissolved in 50–75 ml. hot diluted hydrochloric acid (1:9); the solution is diluted to 200 ml. and 15 ml. hydrochloric acid (sp. gr. 1.19) is added. The solution is cooled to 25° and 25.00 ml. 0.2 *N* bromate–bromide solution is added. Then 10 ml. 25% potassium iodide is added immediately, and the iodine liberated is titrated with standard sodium thiosulfate, adding starch near the end point. One milliliter of 0.2 *N* bromate is equivalent to 0.608 mg. magnesium. Care should be taken in this method to avoid loss of bromine. Closed titration flasks have been described by Greenberg, Anderson, and Tufts,[76] and by Furman and Flagg.[77] Loss of bromine is most serious when one is dealing with small quantities of complex.

The volumetric determination may be carried out in the presence of calcium oxalate[78] (see page 160).

Cerate Oxidation. The method of Nielsen,[9] applied by him to the determination of magnesium in biological materials, and by Gerber, Claassen, and Boruff[10] to the analysis of distilled liquors, is of interest when small quantities of magnesium are to be determined. A satisfactory quantity is 100 μg. of magnesium, although as little as 5 μg. may be determined. The magnesium is precipitated in the usual manner, and collected on a filter stick or centrifuged out. After it has been thoroughly washed with hot water, it is dissolved in 5 ml. perchloric acid. To this solution is added 5.00 ml. (or more, depending on the amount of magnesium) 0.05 *N* ammonium hexanitratocerate in 2 *M* perchloric acid. After the mixture is heated at 96–100° for 10 minutes,

[76] D. M. Greenberg, C. Anderson, and E. V. Tufts, *J. Biol. Chem.*, **111**, 561 (1935).

[77] N. H. Furman and J. F. Flagg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 738 (1940).

[78] J. C. Redmond, *J. Research Natl. Bur. Standards*, **10**, 823 (1933).

the solution is cooled and the excess cerate is titrated with 0.02 *N* ferrous ammonium sulfate, using *o*-phenanthroline ferrous indicator. The excess cerate may also be titrated with 0.02 *N* sodium oxalate, using 0.1% aqueous Setopaline C as indicator. The color change is from pink to colorless, or light yellow.

One mole of magnesium requires 59.7 equivalents of oxidizing agent; hence, 1 ml. 0.05 *N* cerate is equivalent to 20.4 μg. magnesium. Blanks should always be run on the reagents.

0.05 *N* cerate is prepared by dissolving 28 g. ammonium hexanitratocerate in 1 liter 2 *M* perchloric acid (334 g. 60% perchloric acid per liter) and allowing the mixture to stand on the steam bath for 24 hours. The cool solution is centrifuged, decanted into a clean bottle, and standardized by titration with standard sodium oxalate solution. The titration proceeds in the cold in 2 *M* perchloric acid; Setopaline C is the indicator.

2. Precipitation in Alkaline Tartrate Solution[79]

The magnesium solution should contain 3 g. sodium tartrate and 15–20 ml. 2 *N* sodium hydroxide per 100 ml. Magnesium is precipitated by adding 2% alcoholic oxine in slight excess to the cold solution. After it is heated to 60°C. to allow the precipitate to become crystalline, the solution is filtered. The precipitate is washed, first with cold 1% sodium tartrate until the filtrate is colorless, then with cold water. The precipitate is ignited, or analyzed volumetrically. It has been reported[80] that this method affords a good separation from aluminum, but not from iron. Reprecipitation may be necessary in the latter case. It seems that insufficient study has been given this method, and caution is advised in making use of it. The danger of having occluded impurities in the final precipitate, particularly if many foreign ions are present, must not be overlooked.

A. Microdetermination of Magnesium

The determination of magnesium in a large number of substances containing small percentages of the element involves what is substantially a microdetermination. In one respect this is not strictly a microdetermination, because frequently a macro sample is taken. However, in this section are included references to all methods used

[79] Reference 1, page 29.
[80] Reference 2, page 81.

for the determination of small quantities of magnesium; methods given elsewhere deal with appreciably larger quantities. The general manner of precipitating magnesium on the micro scale resembles that already given (page 174), except that the precipitate is filtered cold.

Strebinger and Reif[81] have described a method which works well with pure solutions in the milligram range. If calcium has been separated previously as oxalate, sizable errors are introduced. Cruess-Callaghan[82] reports a microvolumetric method accurate to about 10%.

The gravimetric or volumetric determination of magnesium as a minor constituent has been described for the following classes of materials: blood,[83–89a] natural water and brines,[90, 91] plant ash,[92, 93] soil,[94] biological fluids,[95–98] pharmaceutical preparations,[99, 99a] boiler feed water,[100] and salt.[101] For other micro methods, see page 180, where polarographic methods are described; also see footnote 11*a*, page 162.

B. Determination of Magnesium in Cement, Limestone, and Similar Materials

The direct determination of magnesium in cement, limestone, and

[81] S. Strebinger and M. Reif, *Mikrochemie*, Pregl-Festschrift, 319 (1929).
[82] G. Cruess-Callaghan, *Biochem. J.*, **29**, 1081 (1935).
[83] S. Yoshimatsu, *Tohoku J. Exptl. Med.*, **14**, 1 (1929).
[84] F. Eichholtz and R. Berg, *Biochem. Z.*, **225**, 352 (1930).
[85] C. Bomskov, *Z. physiol. Chem.*, **202**, 32 (1931); *J. Biol. Chem.*, **99**, 17 (1932).
[86] D. M. Greenberg and M. A. Mackey, *J. Biol. Chem.*, **96**, 419 (1932); **99**, 19 (1932).
[87] L. Velluz, *Compt. rend. soc. biol.*, **115**, 253 (1934); *J. pharm. chim.*, **19**, 346 (1934).
[88] M. Arnoux, *Compt. rend. soc. biol.*, **116**, 436 (1934).
[89] M. Delaville and M. Olive, *Ann. chim. anal. chim. appl.*, **20**, 286 (1938).
[89a] G. Glomaud, *Ann. chim. anal. chim. appl.*, **24**, 166 (1942); *J. pharm. chim.*, **1**, 574 (1940–41).
[90] K. von Luck and H. J. Meyer, *Z. angew. Chem.*, **41**, 1281 (1928).
[91] N. V. Komar and R. E. Kirilova, *J. Applied Chem. U.S.S.R.*, **6**, 358 (1933); *Chem. Abstracts*, **28**, 2642 (1934).
[92] M. Javillier and J. Lavollay, *Bull. soc. chim. biol.*, **16**, 1531 (1934).
[93] K. Nehring, *Z. Pflanzenernähr. Düngung u. Bodenk.*, **A21**, 300 (1931).
[94] A. J. Metson, *New Zealand J. Sci. Tech.*, **B22**, 125 (1940).
[95] S. Yoshimatsu, *Tohoku J. Exptl. Med.*, **22**, 263 (1934); *Brit. Chem. Abstracts*, **A**, 380 (1935).
[96] H. J. Hardon and W. Wirjodihardjo, *Chem. Weekblad*, **31**, 662 (1934).
[97] M. Hasegawa, *Tohoku J. Exptl. Med.*, **31**, 422 (1937); *Analyst*, **62**, 904 (1937).
[98] R. Nordbö, *Skand. Arch. Physiol.*, **81**, 258 (1939); *Chem. Abstracts*, **33**, 4623 (1939).
[99] G. J. W. Ferrey, *Quart. J. Pharm.*, **15**, 251 (1942).
[99a] F. K. Bell, *J. Am. Pharm. Assoc.*, **31**, 312 (1942).
[100] W. A. Hough and J. B. Ficklen, *J. Am. Chem. Soc.*, **52**, 4752 (1930).
[101] A. C. Shuman and N. E. Berry, *Ind. Eng. Chem., Anal. Ed.*, **9**, 77 (1937).

similar materials bearing silica, iron, aluminum, and calcium is easily made by the method of Redmond and Bright.[68, 78] Removal of silica is not required, and a single precipitation of iron, aluminum, and calcium is made. The time required for the determination of magnesium in Portland cement, or limestone, need not exceed 1.5 hours for an experienced operator.

To a 0.5-g. sample in a 400-ml. beaker are added 10 ml. water and 10 ml. hydrochloric acid (sp. gr. 1.19). The mixture is heated; coarse particles are ground fine with a stirring rod, and the solution is diluted to 150 ml. To the solution are added 3 drops 0.2% alcoholic methyl red indicator, then ammonia (sp. gr. 0.90) until the solution has a distinct yellow color. Macerated filter paper is added; the solution is boiled for 1–2 minutes, and allowed to stand until the precipitate settles. The precipitate is filtered at once and washed with hot 2% ammonium chloride. To the filtrate is added 1 ml. ammonia (sp. gr. 0.90); the solution is heated to boiling, and 25 ml. hot 4% ammonium oxalate is added. The boiling is continued for 2–3 minutes, and the precipitate is digested on a steam bath for 15–20 minutes.

The solution is allowed to cool to about 70°C.; then 20 ml. oxine solution (25 g. oxine in 60 ml. acetic acid, diluted to 2 liters) is added. This amount of oxine is sufficient for precipitation of the magnesium in a 0.5-g. sample containing not more than 6% magnesium oxide. An excess of ammonia, 4 ml. per 100 ml. of solution, is added and the solution is stirred mechanically for 15 minutes. The precipitate is allowed to settle, collected on a retentive paper, and washed with hot diluted (1:40) ammonia. About 75 ml. hot, diluted (1:9) hydrochloric acid is used to dissolve the precipitate off the filter, which should be thoroughly washed with hot water. The volume of the filtrate and washings should be brought up to 200 ml. After 15 ml. hydrochloric acid (sp. gr. 1.19) is added, the solution is cooled to 25° and 25 ml. 0.2 *N* bromate–bromide reagent is added. Immediately afterward, 10 ml. 25% potassium iodide solution is added, and the iodine is titrated with standard thiosulfate. Near the end point 2 ml. starch indicator is added, and the titration is continued to completion. One milliliter 0.2 *N* bromate is equivalent to 0.608 mg. magnesium. The error in the method as applied to the above-stated classes of materials is substantially less than 1%, and is usually negative.

Miller and McLennan[69] made a critical study of the determination of magnesium in silicate and carbonate rocks, precipitating the mag-

nesium hydroxyquinolate, in much the same manner as described above, after the stepwise separation of silica, "R_2O_3," and calcium. The magnesium complex was weighed after drying at 105° or 160°C.

In the course of a complete analysis, appreciable quantities of neutral salts accumulate in the final solution to be analyzed for magnesium. Among these is ammonium oxalate, which appears to retard the precipitation of magnesium when that element is present to the extent of about 1% (as oxide). It is claimed[69] that smaller quantities of magnesium cannot be precipitated unless oxalate is first destroyed with nitric acid. Large amounts of sodium nitrate have no harmful effect on the precipitation. To insure complete precipitation of 1% magnesium oxide (starting with a 1-g. sample) in the presence of 2 g. or more ammonium oxalate, it is recommended that the solution be cooled for 1–2 hours before filtration and also stirred mechanically for 15 minutes. Best results are obtained by drying the precipitate at 160°. The error, in per cent magnesium oxide, as determined by this method varies from less than 1% for samples containing more than 1% magnesium oxide to about 3% in determinations in which 1% magnesium oxide is present.

Eckstein[102] has described a method for magnesium in dolomite, magnesite, etc., in which the precipitate is analyzed volumetrically. Rabitschek has used oxine for the determination of magnesium in silicates, as has Schoklitsch. In the analysis of magnesite, Raskin and Drozd[103] follow the conventional scheme, precipitating calcium as the oxalate (which is titrated with permanganate) and magnesium from the filtrate with oxine. Shead and Valla[104] precipitate calcium oxalate and magnesium hydroxyquinolate simultaneously, convert them to the mixed oxides, and extract calcium oxide with a 30% cane sugar solution.

C. Determination of Magnesium in Alloys

Methods reported for the determination of magnesium in alloys follow a common pattern. Since the principal constituent is frequently aluminum, the alloy is dissolved as far as possible with sodium hydroxide and the magnesium is precipitated from the residue, after proper treatment, with oxine.

[102] H. Eckstein, *Chem. Ztg.*, **55**, 227 (1931).
[103] L. D. Raskin and I. F. Drozd, *Zavodskaya Lab.*, **5**, 807 (1936); *Chem. Abstracts*, **30**, 7486 (1936).
[104] A. C. Shead and R. K. Valla, *Ind. Eng. Chem., Anal. Ed.*, **4**, 246 (1932).

The general procedure for aluminum–copper–magnesium, aluminum–silicon–magnesium, and aluminum–magnesium alloys is as follows:[105–107a]

The sample, weighing 1–2 g., is treated with 70 ml. 10% sodium hydroxide. When the reaction is complete, the solution is diluted somewhat and filtered. The precipitate is washed with water, and filtrate and washings are discarded. The residue on the filter paper is dissolved in 35 ml. hot 10% sulfuric acid and the paper is washed thoroughly with hot water. The sulfuric acid solution is neutralized with sodium hydroxide, diluted to 150 ml., and heated to boiling. Iron is precipitated by the addition of zinc oxide, after previous oxidation with a few drops of a dilute permanganate solution. Ethyl alcohol sufficient to reduce the excess permanganate is added, and the solution is filtered. If necessary, the filtrate and washings are made up to a definite volume, and an aliquot containing not more than 30 mg. magnesium is taken for precipitation. Otherwise, filtrate and washings are treated as described on page 178 for the precipitation of magnesium. Brook, Stott, and Coates[108] have described a method along similar lines for the determination of magnesium (also antimony, copper, and tin) in aluminum alloys.

A method for the direct determination of magnesium in the presence of zinc has been described[109] in which precipitation of the zinc is prevented by use of potassium cyanide.

The determination of magnesium (and aluminum) in ferrous alloys has been described by Gadeau.[109a] Iron is removed from the solution of the sample by precipitation with hydrogen sulfide in the presence of tartrate; oxine is used to precipitate aluminum, then magnesium, from the filtrate.

D. Polarographic Determination of Magnesium

Methods for polarographic determination of small amounts of magnesium hydroxyquinolate have been devised by Carruthers[110] and by

[105] E. Stokowy, *Aluminium*, **22**, 566 (1940).
[106] R. Bauer and J. Eisen, *ibid.*, **23**, 290 (1941).
[107] A. Robertshaw, *Analyst*, **67**, 259 (1942).
[107a] F. Pitts, *ibid.*, **68**, 133 (1943).
[108] G. B. Brook, G. H. Stott, and A. C. Coates, *Analyst*, **63**, 110 (1938).
[109] S. Y. Fainberg and L. B. Fligelman, *Zavodskaya Lab.*, **5**, 942 (1936); *Chem. Abstracts*, **31**, 335 (1937).
[109a] R. Gadeau, *Rev. met.*, **32**, 398 (1935).
[110] C. Carruthers, *Ind. Eng. Chem., Anal. Ed.*, **15**, 412 (1943).

Stone and Furman.[111] In the first method magnesium hydroxyquinolate is precipitated, filtered, washed, dissolved in hydrochloric acid, and made up to volume with a phosphate buffer. The diffusion current is measured at the first wave, along with the average potential at which the current is measured. (The half-wave potential decreases with decreasing concentration, making this necessary). A calibration curve is constructed, and the method gives results with an error of less than 3% with amounts of magnesium as small as 68 μg.

In the method of Stone and Furman, the magnesium is precipitated by an excess of standard oxine solution and, without removing the precipitate, the excess is determined polarographically. Measurement of the oxine is based on the diffusion current at the first wave ($E_{1/2}$ = 1.39 v. *vs.* S.C.E.). This half-wave potential is substantially constant over the range 0.276×10^{-4} to 2.758×10^{-4} mole of oxine per liter, and the height of the wave is proportional to the concentration.

The general method is as follows: 5 ml. standard oxine solution (0.5 g. per liter in 5% ethanol) and 10 ml. ammonia–ammonium chloride buffer (*p*H 10, 0.036 *M* in ammonium chloride) are placed in a 25-ml. volumetric flask. For determining the original concentration, the flask is filled to the mark and the polarogram taken. For the precipitation, a given amount of unknown is added to the buffer and oxine in the flask. The flask is filled, mixed well, and shaken at frequent intervals for 1–2 hours, depending on the amount of magnesium present. The polarogram is taken on the solution. Magnesium may be determined in tap water or plant materials by this method. The following procedures may be employed.

Tap Water. Fifty milligrams ammonium tartrate is dissolved in the buffer–oxine mixture, to prevent interference by aluminum. A 5-ml. sample of the water is added, and the solution is made up to 25 ml. After the solution has been shaken for two hours and allowed to stand, the polarogram is taken. Good agreement (about 4%) between polarographic methods, colorimetric methods, and gravimetric methods is obtained.

Plant Materials. Samples are dried, ashed, and dissolved in sulfuric acid. The resulting solution is electrolyzed in the Melaven cell and filtered. The filtrate is made up to some standard volume and an aliquot containing about 100 μg. magnesium is taken. The procedure for tap water (above) is then followed.

[111] K. G. Stone and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 596 (1944).

VI. Determination of Zinc

Oxine affords a convenient means of precipitating and determining zinc, which is comparable with the anthranilic acid and quinaldic acid methods. The precipitate forms in acetic acid–acetic buffer, or from alkaline tartrate solution. Employment of the first conditions permits a separation from the alkaline earths, alkali metals, lead, and manganese; the second method enables separation from aluminum, antimony(V), arsenic(V), bismuth, chromium(III), iron(III), lead, and uranium. The precipitate is dried at 160°C. and weighed as $Zn(C_9H_6ON)_2$.[16]

1. Precipitation in Acid Solution[112]

The solution should contain about 50 mg. or less of zinc per 50 ml. and may be slightly acidic. About 4 g. sodium acetate is added, and the *p*H is adjusted to 4.6–5.5 (to separate zinc from magnesium) with acetic acid. The solution is heated to 60–70° and zinc is precipitated by adding an excess of 2% oxine in acetic acid. Heating is continued for a few minutes, and the precipitate is collected and washed with hot water. (With 10 mg. or less zinc, the precipitate is filtered cold). The precipitate of $Zn(C_9H_6ON)_2$, dried at 160°, contains 18.50% zinc. If desired, the precipitate may be analyzed volumetrically as is done for magnesium (see page 175). One milliliter 0.1 *N* bromate is equivalent to 0.817 mg. zinc.

2. Precipitation in Alkaline Tartrate Solution[112]

The determination may be carried out in the presence of elements listed above totalling 200 mg. per 100 ml. Cobalt, manganese, and nickel can be tolerated in amounts up to 50 mg. per 100 ml.; otherwise reprecipitation of the zinc is necessary.

To the zinc solution is added 2–5 g. tartaric acid for each 100 ml. The solution is neutralized to phenolphthalein with strong sodium hydroxide; 10–15 ml. 2 *N* alkali is added in excess, and the solution is diluted to 100 ml. if necessary. Zinc is precipitated from the cold solution with 3% alcoholic oxine reagent. The solution is heated to 60°C. to assist the crystallization of the precipitate; this is then filtered, washed, and analyzed volumetrically.

A. Microdetermination of Zinc

Methods for the microgravimetric and microvolumetric determina-

[112] R. Berg, *Z. anal. Chem.*, **71**, 171 (1927).

tions of zinc have been given.[113–117] These include methods for separating zinc from numerous other elements.

The procedure requires the use of a filter beaker, or a microbeaker and filter stick. The neutral or weakly acid solution containing 1 to 3 mg. zinc in about 1.5 ml. is treated with 2 drops 10% acetic acid and sufficient sodium acetate solution (40%) to raise the *p*H to 5–6, as shown by a universal indicator. The solution is heated until it almost boils, after which 1% alcoholic oxine is added dropwise. From 0.6 to 0.9 ml. should be added per mg. zinc. The mixture is shaken, placed on a boiling water bath for a few minutes, and then allowed to cool for 10 minutes. The precipitate is next filtered, washed with five 1–2-ml. portions of hot water, and dried for 30 minutes at 155°. The precipitate of $Zn(C_9H_6ON)_2$ contains 18.49% zinc.

B. Determination of Zinc in Alloys

In the methods of alloy analysis described, the zinc is determined in the filtrate from the copper, lead, etc., determinations, and no attempt is made to determine zinc directly in the presence of those elements commonly associated with zinc in alloys. Oxine is used rather than phosphate because of the greater speed and convenience it offers, particularly in the volumetric methods. Details are given by Tzinberg,[65] Raskin,[11] Fogelson,[118] Robertshaw,[107] Melnikov,[119] and Mironenko[120] for the determination of zinc in materials such as bronze, babbitt metal, etc.

The separation of zinc and uranium has been studied by Kroupa[121] and by Wiggins and Wood.[122] The amperometric titration of zinc with oxine has been reported.[54]

VII. Other Applications of Oxine

In the following section is given a brief survey of the reactions of

[113] I. M. Kolthoff, *Chem. Weekblad.*, **24**, 606 (1927).
[114] F. Hecht, *Z. anal. Chem.*, **110**, 385 (1937).
[115] C. Cimerman and P. Wenger, *Mikrochemie*, **24**, 153, 162 (1938); **27**, 76 (1939).
[116] C. Cimerman, D. Frank, and P. Wenger, *ibid.*, **24**, 149 (1938).
[117] J. H. Hamence, *Analyst*, **62**, 18 (1937).
[118] E. I. Fogelson and Z. S. Golovleva, *Zavodskaya Lab.*, **7**, 857 (1938); *Chem. Abstracts*, **33**, 499 (1939).
[119] V. V. Melnikov, *Zavodskaya Lab.*, **8**, 1172 (1939); *Chem. Abstracts*, **36**, 3118 (1942).
[120] Z. S. Muchina and M. L. Mironenko, *Zavodskaya Lab.*, **10**, 145 (1941); *Chem. Abstracts*, **35**, 5060 (1941).
[121] E. Kroupa, *Mikrochemie*, **27**, 1 (1939).
[122] W. R. Wiggins and C. E. Wood, *J. Soc. Chem. Ind.*, **53**, 254T (1934).

oxine with other ions. These reactions, and their applications, are considered in detail in Berg's monograph. Sufficient information is given here, largely in the form of references, to enable a general appraisal of their usefulness to be made, and to provide information that may have a bearing on the determination of elements considered in detail in the preceding sections.

Antimony. From a hydrochloric acid solution containing oxine and antimony(III) the yellow complex $Sb(C_9H_6ON)_3$ is precipitated quantitatively as the *p*H is increased to about 6. A basic salt containing oxine is precipitated from tartrate solutions. Since the complex is stable at 105–110°C., it may be used for the gravimetric determination of antimony.[123]

Beryllium. A product of indefinite composition is obtained when a solution containing beryllium and oxine is made alkaline with ammonia. Oxine is useful primarily in separating other elements from beryllium.[124–126]

Bismuth. This element may be precipitated either as $Bi(C_9H_6ON)_3 \cdot H_2O$ from acetic acid or ammoniacal solutions free from halides, or as $C_9H_7ON \cdot HBiI_4$ from acidic solutions. For the separation of bismuth from magnesium a *p*H of 5.2 to 5.4, obtained with an acetate buffer, is recommended.[126a] Results in the precipitation of $C_9H_7ON \cdot HBiI_4$ are apt to be low.[127] The first complex may be dried at 100° (monohydrate), or 140° (anhydrous), or analyzed volumetrically.[123–133]

Calcium. Precipitation is quantitative; however, oxine presents no advantage over the use of oxalate. The solution must be ammoniacal; under these conditions strontium also precipitates, but small amounts of barium are said to cause no difficulty. Oxine is not recommended as a reagent for calcium.[134, 135]

[123] T. I. Pirtea, *Z. anal. Chem.*, **118**, 26 (1939).
[124] M. Niessner, *Z. anal. Chem.*, **76**, 135 (1929).
[125] V. M. Zvenigorodskaya and T. N. Smirnova, *ibid.*, **97**, 323 (1934).
[126] H. V. Churchill, R. W. Bridges, and M. F. Lee, *Ind. Eng. Chem., Anal. Ed.*, **2**, 405 (1930).
[126a] H. G. Haynes, *Analyst*, **70**, 129 (1945).
[127] I. M. Kolthoff and F. S. Griffith, *Mikrochim. Acta*, **3**, 47 (1938).
[128] R. Berg and O. Wurm, *Ber.*, **B60**, 1664 (1927).
[129] R. Berg, *Z. anal. Chem.*, **72**, 177 (1927).
[130] R. Sazerac and J. Pouzergues, *Compt. rend. soc. biol.*, **109**, 370 (1932).
[131] I. M. Korenman, *Z. anal. Chem.*, **99**, 402 (1934).
[132] F. Hecht and R. Reissner, *ibid.*, **103**, 261 (1935).
[133] F. Hecht, W. Reich-Rohrwig, and H. Brantner, *Z. anal. Chem.*, **95**, 159 (1933).
[134] Reference 1, page 40.
[135] L. Korostishevska, quoted in *Chem. Abstracts*, **36**, 3115 (1942).

Chromium. The greenish-yellow complex, $Cr(C_9H_6ON)_3$, is said to precipitate from alkaline solutions in a nonquantitative manner. Chromates may oxidize oxine.[136, 137]

Cobalt. Oxine precipitates cobalt from buffered acetate or alkaline solutions as $Co(C_9H_6ON)_2 \cdot 2\,H_2O$. For concluding the determination, the volumetric method is recommended.[4, 71, 138, 139]

Columbium. Oxine precipitates columbium(V) quantitatively from neutral or weakly acidic oxalate solutions. The precipitate, which contains approximately five moles of oxine per mole Cb_2O_5, may be weighed after drying at 105°C., or titrated with bromate. Tantalum also precipitates under the same conditions.[140]

Gallium and Indium. These elements are precipitated from weakly acid or neutral solutions as the complexes $Ga(C_9H_6ON)_3$ and $In(C_9H_6ON)_3$. The precipitates dry at 110°; they may be analyzed volumetrically as well as gravimetrically.[141, 141a]

Germanium. Precipitation from neutral or slightly acid solutions containing molybdate ion yields $(C_9H_7ON)_4H_4\,[Ge(Mo_{12}O_{40})]$, it is said.[142] The complex may be dried and weighed, or analyzed by the bromate method.

Iron. A greenish-black precipitate is obtained from solutions containing acetic acid and sodium acetate. The complex, $Fe(C_9H_6ON)_3$, is dried at 120° and weighed, or ignited with oxalic acid to Fe_2O_3.[16, 71, 138, 143–147]

Lead. The precipitate, $Pb(C_9H_6ON)_2$, forms from alkaline solution, but as the complex is rather soluble,[148, 149] its use is not recommended.

[136] O. Hackl, *Z. anal. Chem.*, **109**, 91 (1937).
[137] E. Taylor-Austin, *Analyst*, **63**, 710 (1938).
[138] R. Berg, *Z. anal. Chem.*, **76**, 191 (1929).
[139] S. L. Tzinberg, *Zavodskaya Lab.*, **6**, 1007 (1937); *Chem. Abstracts*, **32**, 450 (1938).
[140] P. Süe, *Compt. rend.*, **196**, 1022 (1933).
[141] W. Geilmann and W. Wrigge, *Z. anorg. Chem.*, **209**, 129 (1932).
[141a] G. L. Royer, *Ind. Eng. Chem., Anal. Ed.*, **12**, 439 (1940).
[142] I. P. Alimarin and O. A. Alexeeva, *J. Applied Chem. U.S.S.R.*, **12**, 1900 (1939); *Chem. Abstracts*, **34**, 7777 (1940).
[143] S. L. Tzinberg, *Zavodskaya Lab.*, **4**, 735 (1935); *Chem. Abstracts*, **30**, 985 (1936).
[144] K. Strauss, *Aluminum Non-Ferrous Rev.*, **2**, 418 (1937).
[145] G. J. W. Ferrey, *Quart. J. Pharmacol.*, **15**, 251 (1942).
[146] L. Kampf, *Ind. Eng. Chem., Anal. Ed.*, **13**, 72 (1941).
[147] A. M. Zanko and G. A. Butenko, *Zavodskaya Lab.*, **5**, 415 (1936); *Brit. Chem. Abstracts*, **A1**, 264 (1937).
[148] V. Marsson and L. W. Haase, *Chem. Ztg.*, **52**, 993 (1928).
[149] V. Hovorka, *Collection Czechoslov. Chem. Commun.*, **9**, 191 (1937).

Manganese. Oxine precipitates $Mn(C_9H_6ON)_2 \cdot 2\,H_2O$ from neutral or ammoniacal solutions containing a small amount of a reducing agent such as sulfite or hydroxylamine. Heating at 110° renders the complex anhydrous for weighing; alternatively, it may be ignited with oxalic acid to Mn_3O_4, or determined volumetrically.[71, 138, 145, 150–153]

Molybdenum. The molybdate ion forms insoluble $MoO_2(C_9H_6ON)_2$ with oxine in solutions of *p*H about 3.3 to 7.6. It is best to weigh the precipitate after drying at 130°. Molybdenum may be separated from phosphate by precipitation of the former with oxine in a buffered acetate solution,[71, 154–157] phosphate being determined in the filtrate using molybdate in the ordinary manner.

Nickel. The complex, $Ni(C_9H_6ON)_2 \cdot 2\,H_2O$, is precipitated from acetic acid–acetate buffer, or from more alkaline solutions. The degree of hydration after drying at 105° (and higher) is uncertain, and the volumetric method is recommended.[4, 71, 158, 158a] 1 ml. of 0.1 *N* bromate is equivalent to 0.7335 mg. Ni.

Phosphate. Phosphomolybdic acid forms an insoluble compound with oxine in hydrochloric acid solutions. The formula is said to be $3(C_9H_7ON)H_7\,[P(Mo_2O_7)_6] \cdot 2\,H_2O$; the substance may be dried and weighed (3.06% P_2O_5), or determined volumetrically. Silica, arsenic, and selenium interfere.[159–165a]

Platinum Metals. Divalent palladium (probably platinum also) precipitates with oxine from acid solutions. Under the same conditions

[150] G. S. Smith, *Analyst*, **64**, 787 (1939).
[151] H. W. van der Marel, *Ing. Nederland. Indië*, **8**, No. 10, VII, 110, (1941).
[152] K. Neelakantam, *Current Sci.*, **10**, 21 (1941); *Chem. Abstracts*, **35**, 3554 (1941).
[153] S. L. Tzinberg, *Zavodskaya Lab.*, **6**, 1007 (1937); *Brit. Chem. Abstracts*, **A1**, 213 (1938).
[154] G. Balanescu, *Ann. Chim. Analyt.*, **12**, 259 (1930).
[155] W. Geilmann and F. Weibke, *Z. anorg. allgem. Chem.*, **199**, 347 (1931).
[156] W. Hartmann, *Z. anal. Chem.*, **83**, 470 (1931).
[157] Z. S. Muchina, *Zavodskaya Lab.*, **3**, 1075 (1935); *Brit. Chem. Abstracts*, **B**, 410 (1935).
[158] E. Kroupa, *Mikrochim. Acta*, **3**, 306 (1938).
[158a] H. R. Fleck and A. M. Ward, *Analyst*, **58**, 388 (1933).
[159] R. Berg, *Z. angew. Chem.*, **41**, 611 (1928).
[160] H. T. Bucherer and F. W. Meier, *Z. anal Chem.*, **85**, 331 (1931).
[161] K. Scharrer, *Biochem. Z.*, **261**, 444 (1933).
[162] S. S. Zhukovskaya and S. S. Bernstein, *Zavodskaya Lab.*, **3**, 214 (1934); *Brit. Chem. Abstracts*, **B**, 721 (1934).
[163] I. R. Shik, *Zavodskaya Lab.*, **8**, 1179 (1939); *Chem. Abstracts*, **36**, 3118 (1942).
[164] V. S. Matsevitch, *Zavodskaya Lab.*, **9**, 229 (1940); *Chem. Abstracts*, **36**, 6440 (1942).
[165] V. N. Panfilov, *Chemisation Socialistic Agr. U.S.S.R.*, **9**, 54 (1940); *Chem. Abstracts*, **36**, 6944 (1942).
[165a] P. P. Budnikov and S. S. Zhukovskaya, *J. Applied Chem. U.S.S.R.*, **17**, 165 (1944).

ruthenium(III), rhodium(III), osmium(IV), iridium(IV), and platinum(IV) are not precipitated.[166] The reagent thus might offer possibilities of making separations among the platinum metals.

Rare Earths. The elements of this group (in trivalent form) are precipitated from buffered acetate or ammoniacal tartrate solutions. The precipitates may be dried and weighed, or titrated with bromate, it is reported. Lanthanum, for example, forms $La(C_9H_6ON)_3$, stable at 130°C., and is determined accurately by the gravimetric or volumetric method.[167–169]

Silica. Oxine precipitates silicomolybdic acid from hydrochloric acid solution as $4\ C_9H_6ON \cdot SiO_2 \cdot 12\ MoO_3$. The precipitate is best analyzed volumetrically with bromate.[170–172a]

Thorium. Oxine precipitates thorium at *p*H 4.4 to 8.8 as $Th(C_9H_6ON)_4 \cdot C_9H_7ON \cdot H_2O$, a yellow substance which, upon drying at 150–160°, is converted into the orange $Th(C_9H_6ON)_4$. This compound may be used as a weighing form in both macro- and microanalyses.[173–176] Volumetric methods, which appear not to have been studied, are of potential interest considering the five molecules of oxine per mole of complex.

Titanium. From acetic acid or ammoniacal tartrate solutions oxine precipitates titanium as orange-yellow $TiO(C_9H_6ON)_2 \cdot 2\ H_2O$. The precipitate may be dried at 110°, to give $TiO(C_9H_6ON)_2$, ignited with oxalic acid to TiO_2, or determined volumetrically with bromate.[71, 147, 177–180]

Tungsten. Alkali tungstates form a compound with oxine having

[166] Reference 1, page 83.
[167] T. I. Pirtea, *Z. anal. Chem.*, **107**, 191 (1936); *Bul. Chim., Soc. Romîne Chim.*, **38**, 83 (1938).
[168] G. Mannelli, *Atti congr. intern. chim., 10th Congr. Rome*, **II**, 718 (1938); *Brit Chem. Abstracts*, **A1**, 233 (1940).
[169] R. Berg and E. Becker, *Z. anal. Chem.*, **119**, 1 (1940).
[170] M. I. Volinetz, *Ukraïn, Khem. Zhur.*, **11**, 18 (1936); *Zavodskaya Lab.*, **5**, 162 (1936); *Chem. Abstracts*, **30**, 7497 (1936).
[171] M. I. Volinetz and S. S. Bernstein, *Zavodskaya Lab.*, **5**, 1071 (1936).
[172] L. B. Ginzburg, *ibid.*, **7**, 1041 (1930).
[172a] J. A. Merz, *Svensk. Kem. Tid.*, **53**, 374 (1941); *Chem. Abstracts*, **36**, 1867 (1942).
[173] F. Hecht and W. Reich-Rohrwig, *Monatsh.*, **53–4**, 596 (1929).
[174] F. J. Frere, *J. Am. Chem. Soc.*, **55**, 4362 (1933).
[175] F. Hecht and W. Ehrmann, *Z. anal. Chem.*, **100**, 98 (1935).
[176] P. Wenger and R. Duckert, *Helv. Chim. Acta*, **25**, 1110 (1942).
[177] R. Berg and M. Teitelbaum, *Z. anal. Chem.*, **81**, 1 (1930).
[178] J. Arend and H. Schnellenbach, *Arch. Eisenhüttenw.*, **4**, 265 (1930).
[179] H. Wabnitz, *Sprechsaal*, **65**, 594 (1932).
[180] A. Claassen and J. Visser, *Rec. trav. chim.*, **60**, 213 (1941).

the composition $WO_2(C_9H_6ON)_2$ after drying at 120°. Precipitation should be made at a *p*H of about 6.[4, 71, 181–186]

Uranium. The uranyl ion is precipitated as the orange complex $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$ from very slightly acidic solutions. The precipitate may be dried at 110°, ignited to U_3O_8, or analyzed volumetrically.[4, 71, 122, 173, 174, 187, 187a]

Vanadium. Vanadate ion reacts with oxine in acetic acid solution to form a dark insoluble precipitate, $V_2O_3(C_9H_6ON)_4$, which may be weighed after drying at 120°C., or titrated with bromate. The reaction affords a separation of vanadium from arsenic(V) and chromium(VI).[71, 188–192]

Zirconium. Zirconium nitrate (but not chloride or sulfate) reacts with oxine in buffered acetate solution forming a complex that has the formula $Zr(C_9H_6ON)_4$ after being dried at 130°. The precipitate may be ignited to ZrO_2, or analyzed volumetrically.[193]

VIII. Derivatives of Oxine as Precipitants

Many derivatives of 8-hydroxyquinoline have been studied as analytical reagents. In general they show no unique properties that would make them especially valuable in gravimetric or volumetric analysis, although many cases of enhanced color have been observed, when chromophoric groups are introduced into the hydroxyquinoline nucleus. 5,7-Dibrom-8-hydroxyquinoline has received some attention as a precipitant; its only value would seem to lie in its high molecular weight. This factor is overbalanced by the extremely low solubility of

[181] A. Jilek and A. Rysanek, *Collection Czechoslov. Chem. Commun.*, **5**, 136 (1933); **8**, 246 (1936).
[182] S. Halberstadt, *Z. anal. Chem.*, **92**, 86 (1933); *Compt. rend.*, **205**, 987 (1937).
[183] E. Otero and R. Montequi, *Anales soc. españ fis. quím.*, **33**, 132 (1935).
[184] Z. S. Muchina, *Zavodskaya Lab.*, **7**, 407 (1938); *Brit. Chem. Abstracts*, **B**, 158 (1939).
[185] J. A. Merz, *Svensk. Kem. Tid.*, **53**, 400 (1941); *Chem. Abstracts*, **36**, 1867 (1942).
[186] A. de L. Canticao, *Ministerio trabalho ind. ecom., Inst. nacl. tecnol. (Rio de Janeiro)*, **1941**, 9 pp.
[187] F. Hecht and H. Krafft-Ebing, *Z. anal. Chem.*, **106**, 321 (1936).
[187a] F. Hecht and A. Grünwald, *Mikrochemie ver. Mikrochim. Acta*, **30**, 279 (1943).
[188] A. Jilek and V. Vicovsky, *Collection Czechoslov. Chem. Commun.*, **4**, 1 (1932); *Chem. Listy*, **26**, 16 (1932); *Chem. Abstracts*, **26**, 2138 (1932).
[189] S. L. Tzinberg, *Zavodskaya Lab.*, **1**, 18 (1933); *Brit. Chem. Abstracts*, **A**, 1193 (1934).
[190] R. Montequi and M. Gallego, *Anales soc. españ. fis quím.*, **32**, 134 (1934).
[191] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).
[192] J. M. Bach and R. A. Trelles, *Anales assoc. quím argentina*, **28**, 111 (1940); *Chem. Abstracts*, **35**, 545 (1941).
[193] G. Balanescu, *Z. anal. Chem.*, **101**, 101 (1935).

the compound in aqueous solutions, and applications of the reagent in inorganic gravimetric analysis have not been numerous.

8-Hydroxyquinaldine[194] (2-methyl-8-hydroxyquinoline) has been studied in some detail as a precipitant, and does possess a definite advantage, for certain uses, in that aluminum is not precipitated by the reagent, whereas zinc and other elements are precipitated. The separation of zinc from aluminum and(or) magnesium has been described. In the procedure, the precipitate of zinc 8-hydroxyquinaldinate is weighed, or titrated with bromate–bromide reagent.

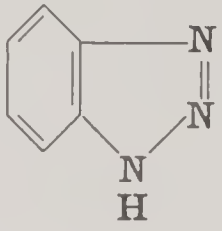
[194] L. L. Merritt and J. K. Walker, *Ind. Eng. Chem., Anal. Ed.*, **16**, 387 (1944).

CHAPTER XII

Miscellaneous Reagents

A number of reagents, none of which warrants discussion in individual chapters, will be considered together in this chapter. The reagents to be included are: benzotriazole, β-furfuraldoxime, hexanitrodiphenylamine, mercaptobenzthiazole, phenylthiohydantoic acid, 8-quinolinecarboxylic acid, and *anti*-"1,5-di"-(*p*-methyoxphenyl)-1-hydroxylamino-3-oximino-4-pentene, a new reagent for tungsten.

I. Benzotriazole



Molecular weight: 119.1
Melting point: 95–97°C.
Solubility: soluble in alcohol, benzene, water
Reagent solution: 2% in water

Benzotriazole precipitates copper quantitatively from a tartrate-acetate solution of *p*H 7.0 to 8.5 as $Cu(C_6H_4N_3)_2$.[1] Also partially or wholly precipitated under the same conditions are cadmium, cobalt, iron(II), nickel, silver, and zinc. Aluminum, antimony(III,V), arsenic(III,V), chromium(III,VI), iron(III), molybdenum(VI), selenium(IV), and tellurium(IV) are not precipitated under these conditions.

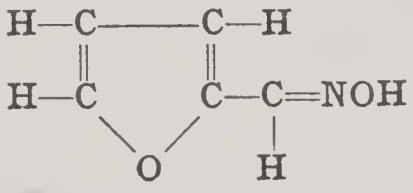
In the absence of interfering elements, the direct gravimetric determination of copper as $Cu(C_6H_4N_3)_2$ is possible. Not more than 20 mg. copper should be precipitated, for which 50 ml. of the 2% reagent solution is required. Precipitation is made from a hot solution; a digestion period should follow. The precipitate, after being collected on a filter crucible and washed with water, is dried for 2 to 3 hours at

[1] J. A. Curtis, *Ind. Eng. Chem., Anal. Ed.*, **13**, 349 (1941).

135–140°C.; it contains 21.22% copper. When interfering elements are present, as in the analysis of steel or copper ores, benzotriazole serves for making the preliminary separation of copper. The copper in the precipitate is then determined iodometrically. In the analysis of steel, the sample is dissolved in nitric acid, and tartaric acid is added later to prevent precipitation of iron when the *p*H is raised.

A particular advantage of the reagent is that it affords a clean separation of copper from antimony, arsenic, molybdenum, selenium, and tellurium, elements which interfere in the iodometric method for copper. This, along with the fact that a nitric acid attack may be used, is of importance in steel analysis. Disadvantages of the reagent are its lack of selectivity, comparatively high cost, and rather narrow *p*H range for precipitation.

II. β-Furfuraldoxime



Molecular weight: 111.1
Melting point: 88–90°C.
Solubility: soluble in alcohol, acetone, water
Reagent solution: 10 g. per 100 ml. alcohol

The single published use for this reagent is for the determination of palladium.[1a] That element is precipitated as the complex salt, $Pd(C_4H_3OCHNOH)_2Cl_2$, in the presence of alkaline earth metals, alkali metals, aluminum, antimony, arsenic(III,V), bismuth, borate, cadmium, cerium(III), cobalt, chromium(III,VI), copper, iron(III), manganese(II,VII), mercury(II), molybdenum(VI), nickel, nitrate, osmium(IV), phosphate, platinum(IV), rhodium(III), ruthenium(III), selenite, sulfate, thorium, tin(II,IV), titanium(IV), tungstate, vanadium(V), zinc, and zirconium ions. Gold(III) must be absent because it reduces the reagent. Cerium(IV) also reacts to form an insoluble compound. Elements whose chlorides are insoluble must likewise be absent. Insoluble sulfate and nitrate complexes of palladium and β-furfuraldoxime are also known; these, however, are readily transformed by an excess of chloride ion into the much less soluble chloride salt.

[1a] J. R. Hayes and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **14**, 491 (1942).

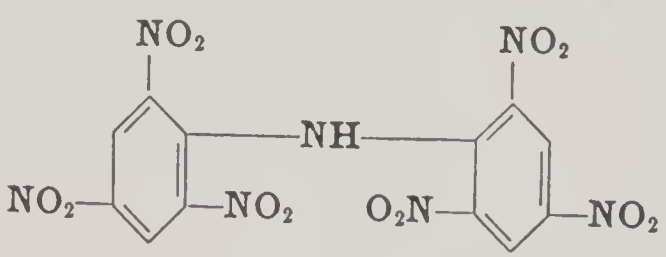
Advantages of β-furfuraldoxime for determining palladium are cited[1a] as: (*1*) higher molecular weight of the complex precipitated than in the dimethylglyoxime method; (*2*) greater ease in filtering the precipitate; and (*3*) use of a water-soluble precipitant.

Determination of Palladium

The palladous chloride solution, containing from 2 to 30 mg. palladium, is diluted to about 100 ml., and the acidity is adjusted to approximately 3% hydrochloric acid (sp. gr. 1.19) by volume; somewhat higher acid concentrations are not harmful. The palladium is precipitated by adding 2 ml. of the alcoholic solution of the oxime to the cold solution. The precipitate is stirred, and is then allowed to settle for an hour or longer.

The precipitate is collected on a weighed filtering crucible, and is washed first with 50 ml. of cold 1% hydrochloric acid, then with the same volume of water. It is then dried for 2 hours at 110°C., and weighed as $Pd(C_4H_3OCHNOH)_2Cl_2$, containing 26.69% palladium. Drying for longer periods of time is not harmful, but the temperature must be kept at or near 110° to avoid decomposition of the precipitate. Results reported [1a] tend to be low by a maximum of about 1%, and high by a maximum of somewhat less than 1%. In general, however, the reported errors are of the order of 0.3% or less.

III. Hexanitrodiphenylamine (Dipicrylamine)



Molecular weight: 439.2
Melting point: 244–246°C.
Solubility: soluble in acetone, ether, methyl amyl ketone; slightly soluble in water; insoluble in dilute mineral acids, carbon tetrachloride, chloroform, dichloroethane, and benzene
Reagent solutions: (*a*) Magnesium dipicrylaminate, 3%: mix 12 g. reagent with 5 g. magnesium oxide, add 400 ml. water; stir, filter after 15–20 hours. (*b*) Sodium dipicrylaminate, 3%: mix reagent with small excess of sodium carbonate, add water to make a 3% solution.

Hexanitrodiphenylamine, or dipricrylamine, is a weak organic acid that forms insoluble normal salts with many metals. Of principal in-

terest is the potassium salt, although aluminum, ammonium, beryllium, bismuth, cesium, chromium, cobalt, copper, iron(III), lead, mercury(I,II), nickel, rubidium, silver, thallium(I), thorium, titanium, vanadium, and zirconium ions form precipitates with the reagent solution. This may be due in part to the precipitation of an hydroxide or a basic salt, for the solution of the reagent as ordinarily prepared is alkaline.

Potassium may be determined gravimetrically by drying the complex at 110° and weighing it,[2, 3] or volumetrically by acidimetric[3, 4] or conductometric[2, 5] titration. Since the potassium salt is appreciably soluble in water and excess reagent solution, precipitation is carried out at 0°, and the precipitate is washed with a saturated solution of the potassium salt at the same temperature. Only in this manner can results be obtained that are not 2–3% low.[3] A careful study of the effect of foreign ions on the precipitation of potassium has been made[3]; the results are summarized in Table XXI.

TABLE XXI[a]

Effect of Foreign Ions on Precipitation of Ten Milligrams of Potassium with Dipicrylamine

Foreign ion	Effect
Ammonium	Precipitated; must be removed by boiling with magnesium oxide, or by adding a slight excess of sodium hydroxide
Sodium	None, up to 100 mg.; double precipitation of the potassium salt is required when up to 250 mg. sodium is present if error less than 1% is desired
Lithium	No error if the lithium/potassium ratio is 1:1
Calcium, magnesium	No error when present in amounts up to 100 mg. each
Barium	Precipitated
Aluminum, chromium, cobalt, copper, iron, nickel, zinc	Precipitated; must be removed by adding magnesium oxide, filtering
Phosphate	Precipitated by the magnesium reagent, but when sodium reagent is used the phosphate/potassium ratio may be 9:1

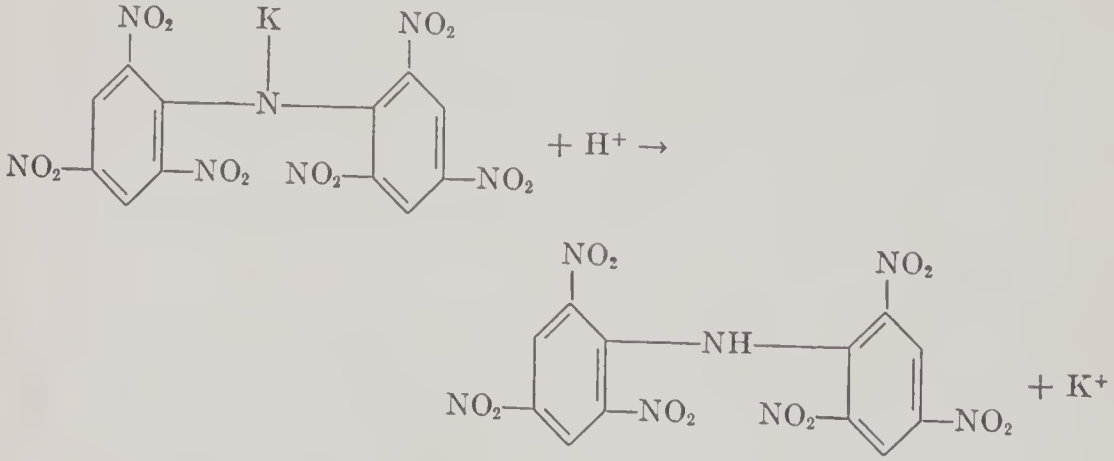
[a] I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939).

[2] A. Winkel and H. Maas, *Angew. Chem.*, **49**, 827 (1936).
[3] I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939).
[4] H. Sueda and M. Kaneko, *Bull. Chem. Soc. Japan*, **16**, 137 (1941); *Chem. Abstracts*, **35**, 6210 (1941).
[5] M. A. Portnov and S. K. Afanas'ev, *Zavodskaya Lab.*, **6**, 1442 (1937).

Determination of Potassium[2]

Gravimetric. A known weight of sample, free from interfering elements, is placed in a weighed 30-ml. crucible containing a small filter stick and glass stirring rod. The volume is adjusted so that the solution contains about 2 mg. potassium per ml., and the solution is neutralized with hydrochloric acid or sodium hydroxide to thymol blue. With constant stirring 50–100% excess of the magnesium reagent is added dropwise. Seven milliliters of the reagent are adequate for 10 mg. potassium. The crucible and contents are cooled for at least 15 minutes in ice water, after which the supernatant liquid is removed by means of the filter stick. The precipitate is sucked as dry as possible, and washed, first with 1 ml. distilled water at 0°, then with three or four 1-ml. portions of a saturated solution of potassium dipicrylaminate in water at 0°, and finally with 0.5 ml. water at 0°C. The filter stick is disconnected and placed in the crucible with the stirring rod. The crucible is wiped clean on the outside, and is then dried with its contents for one hour at 110°, cooled, and weighed. The precipitate of $KC_{12}N_7O_{12}H_4$ contains 8.194% potassium. Results on samples of 1 to 20 mg. show a maximum negative error of 1.8% on a 1-mg. sample. With the larger samples, the error is consistently less than −0.5%.

Volumetric.[3] This method depends in the reaction between an acid and the potassium dipicrylaminate:



A measured amount of standard acid is added, the excess of which is determined with alkali.

The potassium is precipitated and washed as in the gravimetric method. The receptacle used to collect the filtrate is replaced by a clean one (see Fig. 10). With the filter stick connected to the suction

apparatus, acetone is added dropwise down the side of the crucible and the solution is drawn over into the receptacle. After all the precipitate has been dissolved from the crucible and filter stick, and the acetone remains colorless, the receptacle is removed. The acetone solution is diluted with 5–10 ml. water and heated to dissolve the potassium salt. A measured amount of standard acid is added and the

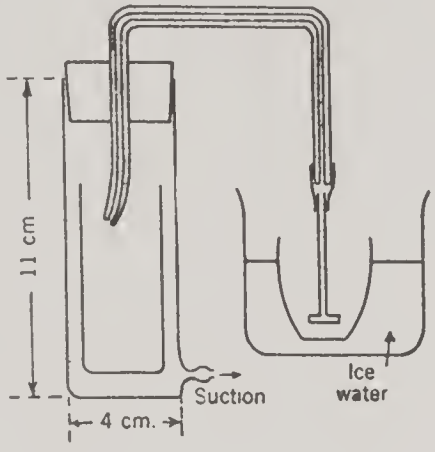


Fig. 10. Filtration assembly.

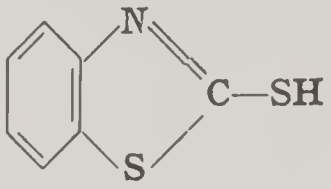
mixture is heated on a steam bath to coagulate the dipicrylamine and expel the acetone. When the odor of acetone is no longer detectable, the mixture is cooled in ice water and the amine is filtered off on a filtering crucible and washed with ice water. The combined filtrate and washings are heated to boiling and titrated while hot with sodium hydroxide, using bromthymol blue as the indicator. One milliliter 0.10 *N* acid is equivalent to 3.91 mg. potassium. Results obtained on 10-mg. samples of potassium show an error of 0.5% or less. The gravimetric and volumetric methods compare favorably with regard to accuracy, and for routine work the volumetric method may be somewhat more rapid.

Other Precipitants for Potassium. Other nitro compounds which have been used in the determination of potassium include picric acid,[6, 7] 2-chloro-3-nitrotoluene-5-sulfonic acid,[8, 9] and 4,6-dinitrobenzofuroxan.[10] As before, the potassium, rubidium, cesium, and ammonium salts are characterized by a much lower solubility in water than is shown by the lithium and sodium salts, although frequently

[6] A. Bolliger, *J. Biol. Chem.*, **107**, 229 (1934).
[7] E. R. Caley, *J. Am. Chem. Soc.*, **53**, 539 (1931).
[8] H. Davies and W. Davies, *J. Chem. Soc.*, **123**, 2976 (1923).
[9] V. H. Dermer and O. C. Dermer, *J. Am. Chem. Soc.*, **60**, 1 (1938).
[10] H. Rathsburg and A. Scheuerer, *Die Chemie*, **56**, 123 (1943).

the solubility of the potassium salt is still too great for making quantitative precipitations from aqueous solutions.

IV. Mercaptobenzthiazole



Molecular weight: 167.2
Melting point: 180°C.
Solubility: slightly soluble in alcohol, sodium hydroxide; insoluble in water
Reagent solution: 5% in alcohol

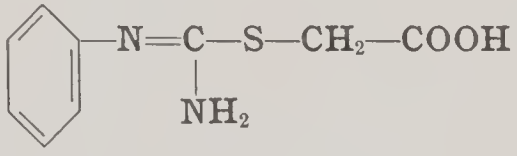
Mercaptobenzthiazole combines with numerous inorganic ions to yield precipitates that have been used in gravimetric analysis.[11, 12] From a weakly acidic solution the reagent precipitates copper, whereas —from solutions of higher *p*H—bismuth, cadmium, gold, lead, mercury, silver, and thallium ions are precipitated. Under conditions used for the precipitation of copper, the alkali metals and alkaline earths, cadmium, cobalt, manganese, nickel, and zinc are not precipitated and copper presumably may be determined in their presence. The copper complex is always contaminated by excess precipitant, and hence must be ignited before final weighing. Complete conversion to copper oxide is difficult, however, for some sulfur is always retained in the precipitate as sulfate.[13] It thus seems necessary, in order to obtain results of highest accuracy, to determine the copper in the ignited precipitate by an established procedure such as the iodometric or electrodeposition method.

The gravimetric determination of copper is carried out as follows. The warm solution containing copper is treated with an excess of the alcoholic reagent. After stirring and heating to cause coagulation, the orange-yellow precipitate is filtered, washed with hot water, dried and ignited to CuO. Subsequent treatment of the precipitate depends on the accuracy required in the determination: the volumetric iodide method is preferred. The same method may be used for the gravimetric determination of mercaptobenzthiazole, employing an excess of copper ion as the precipitant.

[11] G. Spacu and M. Kuras, *Z. anal. Chem.*, **102**, 24, 108 (1935); **104**, 88 (1936).
[12] M. Kuras, *Chem. Obzor*, **13**, 95 (1938).
[13] L. Springer, *Dissertation*, Technische Hochschule, Munich, 1931.

Cadmium is precipitated from an ammoniacal solution as an ammoniated derivative of $Cd(C_7H_4NS_2)_2$. To the solution containing cadmium is added excess ammonia, followed by an ammoniacal solution of the reagent. After stirring, the precipitate is collected on a filter crucible, washed with diluted ammonia, and dried for 1 hour at 110° C. The precipitate of $Cd(C_7H_4NS_2)_2$ contains 25.30% cadmium. Cadmium may be determined in this manner in the filtrate from a copper precipitation using the same reagent.

V. Phenylthiohydantoic Acid



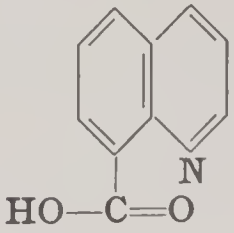
Molecular weight: 210.2
Melting point: 157–158°C.
Solubility: soluble in acetone; slightly soluble in alcohol and water
Reagent solution: saturated alcoholic or aqueous solution

Like other reagents containing sulfur, phenylthiohydantoic acid combines with the metals of the acid hydrogen sulfide group (antimony, bismuth, cadmium, copper, lead, and mercury), as well as with cobalt, iron, and nickel. Presumably the inner-complex type of salt is formed, but the precipitates are never of sufficiently definite composition to permit direct drying and weighing; they are always ignited prior to the final weighing. Phenylthiohydantoic acid has received attention as a reagent for the determination of cobalt, which is precipitated in a slightly ammoniacal solution.[14] Under proper conditions, cobalt may be separated from aluminum, arsenic, calcium, chromium, iron, magnesium, manganese, molybdenum, titanium, tungsten, uranium, vanadium, and zinc. Nickel is partially precipitated, but the complex is more soluble in ammonia, up to a certain concentration, than is the cobalt complex, and consequently a partial separation may be made. The cobalt complex is ignited to "Co_2O_3," which is weighed; or it may be dissolved in acid, whereupon its cobalt content may be determined electrolytically. The cobalt may also be determined volumetrically by oxidation with perborate or peroxide, followed by reduction to the cobaltous ion. The method has been applied to the determination of cobalt in steel, using citrate ion to prevent, as far as possible, the coprecipitation of iron.

[14] H. H. Willard and D. Hall, *J. Am. Chem. Soc.*, 44, 2219, 2226, 2237 (1922).

A method for the precipitation of copper has also been given,[15] but since the compound must be ignited and dissolved, and the copper must then be determined by conventional methods, there is no advantage over the use of other organic precipitants.

VI. 8-Quinolinecarboxylic Acid



Molecular weight: 173.2
Melting point: 187°C.
Solubility: slightly soluble in water; soluble in acetone, alcohol, ether
Reagent solution: saturated aqueous solution

The use of this reagent for the gravimetric determination of copper has been reported.[16] Under the conditions used, gold and silver are said to precipitate with the reagent, where cadmium, cobalt, lead, mercury, nickel, and zinc do not. The optimum *p*H for combination with copper is 3.5 to 4.0; the complex, $Cu(C_{10}H_6NO_2)_2$, is precipitated under these conditions and may be weighed directly after being dried at 110–120°C.

In solutions containing only copper (up to 50 mg. in 100 ml.) the determination is carried out as follows: the solution is neutralized with ammonia until the deep blue color of the tetrammine cupric ion appears; the color is discharged by 3 *N* acetic acid, of which a 5-drop excess is added. Copper is precipitated from the boiling solution by addition (with stirring) of 60 ml. reagent solution. After being allowed to cool for 2 hours, the precipitate is collected on a filter crucible, fine porosity, washed first with diluted (1:10) reagent solution and then with a little cold water, and dried to constant weight at 110–120°C. The precipitate contains 15.58% copper.

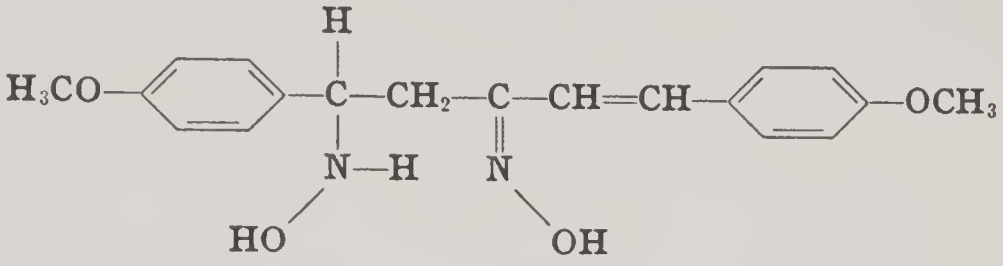
When cadmium or zinc is present, ammonia is added to incipient precipitation of the respective hydroxide. The solution is then acidified to litmus with 0.1 *N* acetic acid, heated to boiling, and treated as above.

The error in the determination when only copper is present is about

[15] H. H. Willard and D. Hall, *J. Am. Chem. Soc.*, 44, 2253 (1922).
[16] J. R. Gilbreath and H. M. Haendler, *Ind. Eng. Chem., Anal. Ed.*, 14, 866 (1942).

0.1%, and is almost the same in the presence of a twofold excess of cadmium or zinc.

VII. Anti-1,5-di-(*p*-methoxyphenyl)-1-hydroxylamino-3-oximino-4-pentene



Molecular weight: 342.3
Melting point: 156–157°C.
Solubility: soluble in acetic acid, acetone, benzene, dioxane, ethanol, ethyl acetate, ethyl ether; insoluble in water, petroleum ether
Reagent solution: 0.76% in ethanol

This reagent has recently been introduced[17] for the gravimetric determination of tungsten. In acidic solution the compound combines with the tungstate ion in the ratio of one molecule of reagent to one molecule of tungstate to form an insoluble complex, the solubility of which is less than 1 mg. per liter (in water) at 25°. The organotungstate precipitate cannot conveniently be weighed directly, but must rather be ignited to tungstic oxide, WO_3. Coprecipitation of the reagent itself and possible precipitation of some of the tungsten as tungstic acid make this procedure necessary.

Tungsten is quantitatively precipitated when the acidity is less than *p*H 1, preferably that obtained in 0.2 *N* hydrochloric acid. Above *p*H 5 no precipitation occurs, and between *p*H 1 and *p*H 5 the precipitation is incomplete. Under the conditions used for precipitating tungsten, the only ions that interfere by forming insoluble compounds are: gold(III), cerium(IV), iridium(IV), iron(III) (slight interference), tin(II,IV), molybdenum(VI), uranium(VI), and osmium(VIII).

Procedures have been given for the determination of tungsten in solutions, steels, alloys, and ores. Results obtained in the analysis of solutions indicate that the new reagent is as satisfactory as cinchonine with regard to accuracy. Favorable results are also obtained in the analysis of standard alloy, steel, and ore samples.[17] The following procedures are recommended.

[17] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 45 (1944).

A. Determination of Tungsten in Ores[17]

"Transfer to a 400 ml. beaker 1 gram of sample which has been ground in an agate mortar to 200-mesh or finer and dried to constant weight at 105°C. Unless the sample is ground to 200-mesh or finer, a protective layer of precipitated tungstic acid may coat the particles, preventing the hydrochloric and nitric acids from coming in contact with all the unreacted material. This is especially true with ferberite and wolframite, which are difficult to decompose. If sufficient hydrochloric acid is used and the temperature is held at approximately 75°C., the formation of tungstic acid on the particles may be avoided. Serious error may be introduced by this effect if samples of particles size much larger than 200-mesh are used. The magnitude of the error depends on the mineral being analyzed. Scheelite, $CaWO_4$, and hubnerite, $MnWO_4$, are easily decomposed by the hydrochloric–nitric acid treatment, in which case the error is small: ferberite, $FeWO_4$, and wolframite, $(FeMn)WO_4$, being much more difficult to decompose, require very small particle size.

"Add 5 ml. of distilled water and rotate the beaker so as to distribute the sample evenly over its bottom. Add 100 ml. of hydrochloric acid (sp. gr. 1.19), cover the beaker with a watch glass, and heat for one hour at a temperature not exceeding 60°. Stir occasionally to break up formations of crusts and to facilitate contact of the acid with all particles of the sample. Raise the watch glass on glass hooks and cautiously boil to a volume of about 50 ml. Break up the material on the bottom of the beaker with a glass stirring rod. Add 40 ml. of hydrochloric acid and 15 ml. of nitric acid and again boil the solution to about 50 ml. Stir up the caked matter again, add 5 ml. of nitric acid, and boil to 10 or 15 ml Dilute to 250 ml. with hot water and heat just below boiling for 30 minutes. Allow to cool to room temperature and add 25 ml. of alcoholic reagent solution slowly with constant stirring. Allow the precipitate to settle for about 2 hours and test the supernatant liquid with a few drops of the reagent for complete precipitation of tungsten." More reagent is added if an orange precipitate forms.

"After the precipitate has settled for at least 2 hours (or overnight if convenient) filter by decantation through an 11-cm. ashless filter paper. Wash the precipitate several times with reagent wash solution (prepared by diluting 20 ml. of hydrochloric acid (sp. gr. 1.19) to 1 liter and adding 1 ml. of the reagent solution).

"Transfer the precipitate to an ashless filter paper and moderately scrub the beaker by means of a rubber policeman to remove, as far as possible, any precipitate adhering to the walls of the beaker. It is not necessary at this point to attempt to remove all the finely divided tungstic acid adhering to the walls of the beaker, since the main precipitate, after it is washed, is to be transferred back to this beaker and all the precipitated tungsten redissolved.

"Wash with the prepared wash solution. Repeat several times and set aside the combined filtrate and washings. Test the filtrate with a few drops of reagent solution for complete precipitation of the tungsten. It is rare that any is found in this filtrate. Transfer the filter paper containing the washed precipitate to the original beaker and add 6 ml. of concentrated ammonium hydroxide. Shred the filter paper to a uniform pulp by means of a glass stirring rod, cover the beaker, and warm gently for a few minutes. Stir the pasty mass with the rod, then wash down the inside of the beaker with warm dilute ammonium hydroxide (1:9) containing 10 grams of ammonium chloride per liter. Warm again and stir thoroughly. Filter through an 11-cm. ashless filter paper and collect the filtrate in a 400 ml. beaker. Wash the original beaker and residue several times with the warm dilute ammonium hydroxide solution; between washings squeeze as much liquid from the fibers of the pulp as possible. Wash the beaker and residue with several small portions of hot 95 per cent ethanol to dissolve any organotungstate that has not been decomposed by the ammonium hydroxide treatment. Follow with a final washing with the warm dilute ammonium hydroxide solution. Keep the volume of the liquid as small as possible. Reserve the residue of filter fiber for further recovery of traces of tungsten.

"Evaporate the filtrate to a volume of about 50 ml.; add 20 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid; cover and cautiously boil to a volume of 10–15 ml. If any organic residue is still present and tends to adhere to the walls of the beaker, it may be decomposed by the addition of more hydrochloric and nitric acids in the same ratio as above. Dilute the solution to about 250 ml. with water and allow it to cool slowly to room temperature. Add the alcoholic reagent solution until the color of the precipitate, as it forms, indicates complete precipitation of the tungsten. Allow the precipitate to settle and filter through an 11-cm. ashless filter paper; wash thoroughly with reagent wash solution. If the filtrate has a clear

yellow tint, precipitation is complete. If it is colorless, more reagent must be added to complete the precipitation. The washed precipitate is the main precipitate and is to be ignited with the very small amounts of tungsten that may be obtained in the procedure described in the following paragraphs.

"Any tungsten that may not have been recovered is contained in the reserved residue of filter fiber, in combination with iron or alumina or with small amounts of reagent that were not completely dissolved. This combined tungsten may be dissolved by digesting the filter paper and residue of fiber with warm dilute hydrochloric acid (1:9). Filter and wash the residue with small amounts of hot 0.5% ammonium chloride solution and the warm dilute ammonium hydroxide wash solution, collecting all in the same vessel. Acidify the filtrate with hydrochloric acid until it is approximately 0.2 *N* and then slowly add 5 to 10 ml. of the alcoholic reagent solution. Any precipitate obtained should be filtered and washed with the reagent wash solution. Reserve the washed precipitate and ignite later with the main one already obtained.

"The residue that remains is usually free from tungsten. To be positive, ignite it in a porcelain crucible, transfer the ash to a platinum crucible, and volatilize the silicon by treating it with hydrofluoric and sulfuric acids. Fuse the residue with as little sodium carbonate as possible, cool, and extract the melt with water. Filter, and acidify the filtrate with hydrochloric acid, boil to expel carbon dioxide, and add dropwise some of the reagent solution to test for the possible presence of tungstate ions. If the precipitate is orange, upon the addition of the first few drops of reagent, filter it off, wash with the reagent wash solution and ignite with the two residues already obtained.

"Place the papers containing the main precipitate and the two recoveries in a weighed platinum crucible and heat at a temperature below a dull red heat until all the carbon has been burned off. Cool, add a few drops of hydrofluoric acid to the residue, add a drop of sulfuric acid, and evaporate to dryness over a water or sand bath. Reignite in order to get the weight of WO_3 free from SiO_2."

The tungstic oxide is then examined for traces of iron, molybdenum, and phosphorus. The iron is separated by fusion with Na_2CO_3, dissolving the melt in hot water, and filtering. Mo is determined colorimetrically in the filtrate.[18] The amount of P is usually negligible.

[18] F. S. Grimaldi, and R. C. Wells, *Ind. Eng. Chem., Anal. Ed.*, **15**, 315 (1943).

B. Determination of Tungsten in Alloys and Metals[17]

"Treat 1 gram of the finely divided metallic sample with 5 ml. of hydrofluoric acid in a large covered platinum crucible or dish. After the initial effervescence has ceased, add nitric acid dropwise until the metal has dissolved. Add 15 ml. of sulfuric acid (1:1), transfer the vessel to a sand bath, and heat cautiously until dense fumes of sulfur trioxide are evolved freely. Perchloric acid may be substituted for sulfuric acid if desired. In this case, add 15 ml. of perchloric acid (60 percent) after the hydrofluoric–nitric acid treatment and heat cautiously to dense fumes. Cool, dilute, and transfer in the same manner as when sulfuric acid is used. The use of perchloric acid shortens slightly the time necessary for this part of the analysis, but otherwise offers no particular advantage.

"Allow to cool and transfer the contents to a 400 ml. beaker by washing the platinum vessel with a fine stream of water. Wipe the vessel with a small piece of ashless filter paper and transfer it to the beaker. Rinse the vessel with a little warm ammonium hydroxide (1:1), a little water, then a little hot hydrochloric acid (1:1). Repeat the treatments with ammonium hydroxide, water, and hydrochloric acid, adding all rinsings to the 400 ml. beaker. Dilute the contents of the beaker with water to about 150 ml. Add 10 ml. of hydrochloric acid (sp. gr. 1.19), cover with a watch glass supported on glass hooks, and boil cautiously for at least 5 minutes. Remove the source of heat and dilute the contents to about 350 ml. with water. Allow to cool and add slowly, with constant stirring, 15 to 20 ml. of alcoholic reagent solution. Allow the precipitate to settle for about 2 hours, and test the supernatant liquid for complete precipitation of the tungsten. If an orange precipitate forms upon the addition of more reagent, precipitation is incomplete. If the precipitate is almost white, separation of tungsten is complete.

"When the precipitate has completely settled, filter by decantation through an 11-cm. ashless paper. Wash the precipitate several times with reagent wash solution, ignite the paper and residue, in the platinum vessel in which the sample was treated originally, at a temperature below dull red heat until all of the carbon is consumed. Add a few drops of nitric acid and evaporate to dryness on a water or sand bath. Ignite to constant weight at a temperature not exceeding 750°C. This is the weight of the impure tungstic oxide. Add about 5 grams of sodium carbonate and heat until a clear melt is obtained. Rotate the

fused mass in the vessel until it solidifies around the wall. When cool, dissolve the melt in hot water, filter through an 11-cm. ashless paper, and wash thoroughly with hot water. Place the filter in the crucible and ignite again. Repeat the sodium carbonate fusion on the small residue, using a proportionately smaller amount of carbonate. Cool and dissolve in the same manner as before. Filter and wash thoroughly to remove all traces of sodium carbonate. Ignite in the same platinum vessel, cool, and weigh. Subtract the weight of this oxide residue from that of the original impure tungstic oxide. Calculate the percentage of tungsten from the corrected weight of tungstic oxide."

If molybdenum is present, the extent of its contamination of the tungsten precipitate can be determined in the sodium carbonate extract. This is best done colorimetrically.[18]

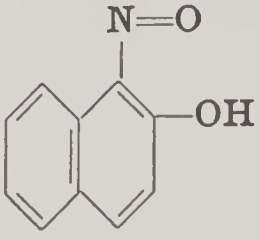
VIII. Other Reagents

Some other reagents which have been reported recently, but which have not as yet been extensively studied, include: 4-hydroxybenzthiazole,[19] for the determination of copper, nickel, and zinc; isonitroso-3-phenylpyrazolone,[20] for the determination of copper; and 2-chloro-7-methoxy-5-thiolacridine,[21] for the determination of mercury and copper.

[19] H. Erlenmeyer and E. H. Schmid, *Helv. Chim. Acta*, **24**, 1159 (1941).
[20] V. Hovorka and J. Vorisek, *Chem. Listy*, **36**, 73 (1942); *Chem. Abstracts*, **37**, 4321 (1943).
[21] S. J. DasGupta, *J. Indian Chem. Soc.*, **18**, 43 (1941).

CHAPTER XIII

α-Nitroso-β-Naphthol



Molecular weight: 173.2
Melting point: 109°C.
Solubility: soluble in acetic acid, alcohol, benzene; insoluble in water
Reagent solution: prepared by dissolving 10 g. α-nitroso-β-naphthol in 500 ml. hot (1:1) acetic acid, filtering when cool*

The principal use of α-nitroso-β-naphthol has been in the gravimetric determination of cobalt; indeed, this is one of the oldest of all methods employing organic reagents. Other uses of the reagent have been found in the gravimetric determination of copper, iron(III), palladium, and zirconium.

When employed in a weakly acidic solution, the reagent will combine with bismuth, chromium(III), silver, tin(IV), titanium, tungsten(VI), uranium(VI), and vanadium(V) ions in addition to those already mentioned. Elements whose ions do not precipitate under these conditions include aluminum, antimony, arsenic, beryllium, cadmium, calcium, lead, manganese, mercury, nickel, the trivalent rare earths, and zinc, as well as the alkaline earths, alkali metals, and phosphate ion.

The complex that is formed when a solution of the potassium salt of the reagent is added to a neutral cobalt solution is reported[1] to be $Co[C_{10}H_6O(NO)_2]_2$. This red-brown precipitate can be converted into

* It has been reported (H. A. Fales and F. Kenny, *Inorganic Quantitative Analysis*, Appleton-Century, New York, 1939, p. 349) that α-nitroso-β-naphthol may contain a substance that precipitates nickel, but that this material settles from solution as a brown precipitate after standing for several days. A blank to test whether a particular lot of the reagent precipitates nickel is recommended.

[1] M. Ilinski and G. von Knorre, *Ber.*, **18**, 699 (1885).

a purple salt, $Co[C_{10}H_6O(NO)]_3$, by heating with dilute acids. The same substance precipitates when an alcoholic or acetic acid solution of the reagent is added to an acidic cobalt solution, but, since the composition of the precipitate cannot be controlled under all conditions, it is ignited and the cobalt is weighed as oxide, sulfate, or metal.

Mayr and Feigl[2] have reported the discovery of a compound, said to be $Co[C_{10}H_6O(NO)]_3 \cdot 3\,H_2O$, which may be precipitated uniformly, and may be dried at 130°C. for weighing. To obtain this compound they first treated the cobalt with alkaline peroxide to precipitate cobaltic hydroxide $Co(OH)_3$, which was then dissolved in acid, supposedly to form free Co^{+++} ions. The cobalt in this oxidation state was then precipitated with α-nitroso-β-naphthol.

Kolthoff and Langer[3] have studied the precipitation of cobalt with α-nitroso-β-naphthol by means of amperometric titration. From a neutral cobalt solution, they found that the red-brown compound $Co[C_{10}H_6O(NO)]_2$ is precipitated by the potassium salt of the reagent. When precipitation was made from a buffer 0.1 *M* in acetate ion and 0.2 *M* in acetic acid, a purple-red precipitate of either $Co[C_{10}H_6O(NO)]_4$ or $Co[C_{10}H_6O(NO)]_2 \cdot 2\,C_{10}H_7O(NO)$ was formed. From an ammoniacal solution containing ammonium chloride, a dark brown precipitate having an approximate composition $Co[C_{10}H_6O(NO)]_3$ was obtained, although the results were variable due to air oxidation of the cobalt in the ammoniacal solution. The work of Kolthoff and Langer also indicates that the precipitate obtained under conditions prescribed by Feigl and Mayr contains no trivalent cobalt, and that the precipitate generally has the composition $Co[C_{10}H_6O(NO)]_4$ or $Co[C_{10}H_6O(NO)]_2 \cdot 2\,C_{10}H_7O(NO)$. It was found, however, that the composition of the complex dried at 135°C. was variable, depending on the conditions of precipitation. This would introduce an uncertainty into the use of the complex obtained under these conditions as a weighing form for cobalt. Other workers[4] have encountered difficulties in the use of this weighing form. In view of the uncertain composition of the cobalt α-nitroso-β-naphthol precipitates, it seems best to convert them to metal, oxide, or sulfate for final weighing.

The composition of the copper(II) salt formed in acetic acid–acetate or ammonia–ammonium chloride buffers is established as

[2] C. Mayr and F. Feigl, *Z. anal. Chem.*, **90**, 15 (1932).
[3] I. M. Kolthoff and A. Langer, *J. Am. Chem. Soc.*, **62**, 3172 (1940).
[4] F. Hecht and F. Korkisch, *Mikrochim. Acta*, **3**, 313 (1938); *Chem. Abstracts*, **32**, 7853 (1938).

$Cu[C_{10}H_6O(NO)]_2$ by the amperometric titration.[3] The palladium(II) salt formed in the acetate buffer is $Pd[C_{10}H_6O(NO)]_2$. In gravimetric work, both complexes are generally ignited, either to cupric oxide, or to a palladium oxide which is subsequently reduced in hydrogen for weighing as the metal.

I. Determination of Cobalt

A. General

The solution to be analyzed should contain none of the interfering elements listed on page 207, and should contain no more than 0.1 g. cobalt and 0.2 g. nickel. Aluminum and zinc are known to give no interference.[2,5,6] The metals should be present as sulfates or chlorides, and the solution should be acidic with hydrochloric acid. The solution is diluted to about 200 ml., and sufficient hydrochloric acid is added to make a total of about 5 ml. of the concentrated acid in the solution. The solution is heated to 80–90°C., and freshly prepared α-nitroso-β-naphthol reagent (page 207) is added hot until precipitation is complete. The precipitate is allowed to settle, and the solution is tested for completeness of precipitation, adding more reagent if necessary. The precipitate should stand for two hours or more; then the clear solution is decanted through a paper or a filtering crucible. The precipitate is washed by decantation with hot (1:2) hydrochloric acid and transferred to the filter, where it is washed with hot water until free from acid. If the amount of cobalt does not exceed a few milligrams, the precipitate is dried, and ignited carefully in an oxidizing atmosphere at 750–850°C. After cooling, the precipitate is weighed as cobaltocobaltic oxide, Co_3O_4. Alternatively, the precipitate may be reduced in a stream of hydrogen, and cobalt may be weighed as the metal.

With quantities of cobalt larger than a few milligrams, the determination should be concluded as follows: the dried precipitate is covered with oxalic acid, and heated over a low flame until the organic matter has burned off. (With larger amounts of the nitrosonaphthol complex, sudden decomposition may result in mechanical losses during the ignition process.) The precipitate is ignited strongly for a few minutes, allowed to cool, and treated with a few drops of concentrated nitric acid to convert the oxide to nitrate. The excess nitric acid is

[5] J. E. Clennel, *Mining Mag.*, **36**, 270 (1927).
[6] L. Philippot, *Bull. soc. chim. Belg.*, **44**, 140 (1935).

expelled by evaporating carefully, then sufficient sulfuric acid is added to convert the nitrate to sulfate. The acids are carefully evaporated, finally to fumes of sulfur trioxide. The excess sulfuric acid is removed by careful heating, and the precipitate of cobalt sulfate is ignited for a short time at 450–500°C. Small amounts of cobalt may be weighed directly as the sulfate. If the cobalt sulfate weighs more than one milligram, it should be moistened with water and heated again to expel free sulfuric acid.[7] The final weighing form is cobaltous sulfate, $CoSO_4$, containing 38.03% cobalt.

The determination may be concluded by electrolysis in place of the method just given. The cobalt sulfate, obtained free from nitric acid as above, is dissolved in 150 ml. water. Twenty grams of ammonium sulfate and 35 ml. concentrated ammonium hydroxide are added, and the cobalt is deposited on platinum cathodes using a direct current density of 0.2 to 0.3 amp. per dm.^{2}. The electrolysis requires from six to eight hours. The electrodes are washed with alcohol or acetone and dried. The cobalt is weighed as metal. The time of electrolysis may be considerably shortened by the use of a rotating anode, or some other means for vigorous stirring and higher current densities (0.5 to 2 amp. per dm.^{2}). The solution is tested for completeness of deposition by withdrawing small portions and testing with ammonium sulfide.

B. Determination of Cobalt in Steel*

1. Cobalt Steel

"Transfer 1 gram of sample to a 400 ml. beaker, add 25 ml. of diluted (1:1) hydrochloric acid, heat, and when decomposition is complete, add 5 ml. of diluted nitric acid (1:3) to oxidize the iron. If tungsten is present, the digestion must be continued until all of the tungsten has been converted to yellow tungstic acid. Evaporate until salts begin to separate (about 5 ml.). Add 100 ml. of hot water and digest on the steam bath for about five minutes. Dilute the solution to about 200 ml., and add a freshly prepared suspension of zinc oxide" (50 g. of the powdered reagent in 300 ml. water, shaken thoroughly) "in portions of about 5 ml. until the iron is precipitated, and a slight excess of zinc oxide is present. Shake thoroughly after each addition of the precipitant and avoid a large excess. When sufficient zinc oxide

* Method of the American Society for Testing Materials.

[7] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1928, p. 325.

has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is also indicated by a slightly white and milky supernatant liquid. Allow the precipitate to settle for a few minutes and filter the solution through a rapid 12.5 cm. filter paper (disregarding any zinc oxide that may pass through the paper). Wash the beaker and the precipitate on the filter paper three times with cold water. Reserve the filtrate and washings. When the filter has drained, transfer the paper and precipitate to the beaker in which the precipitation was made, add 12 ml. of hydrochloric acid, and stir the paper to a pulp. The iron should now be in solution; if it is not, add more hydrochloric acid, avoiding a large excess. Dilute the solution to 200 ml. and repeat the precipitation with zinc oxide. Filter on a 15 cm. paper and wash four or five times with cold water.

"For routine work a single precipitation will often suffice. In this case take a two-gram sample, dilute the solution to exactly 500 ml. after the addition of the zinc oxide, mix thoroughly, and filter through a dry filter into a 250-ml. measuring flask (equivalent to 1 gram of sample). With one precipitation by zinc oxide, results for cobalt in high speed steels will be from 0.1 to 0.3% low through retention of cobalt by the bulky precipitate.

"To the combined filtrates and washings from the zinc oxide separation, add 10 ml. of hydrochloric acid and adjust the volume to about 400 ml. Heat the solution to boiling, add 8 ml. of α-nitroso-β-naphthol solution plus 3 ml. in addition for every 0.01 g. of cobalt present. Allow the solution to cool for one half hour or longer," and conclude the determination as described on page 209. If less than 0.01 g. cobalt is involved in the determination, the cobaltocobaltic oxide, Co_3O_4, is weighed directly; otherwise the oxide is reduced in hydrogen and weighed as the metal, or presumably determined electrolytically."

Consideration must also be taken of the fact that in cobaltocobaltic oxide precipitates obtained from high molybdenum or copper steels, up to 0.5 mg. of these metals may be present. The contaminants are determined colorimetrically, and suitable corrections are made. Varying amounts of nickel may be found in the cobalt precipitate, although the errors are serious only when nickel greatly preponderates in the steel. In such cases the ignited oxide may be dissolved in hydrochloric acid and the cobalt reprecipitated with α-nitroso-β-naphthol. It is recommended that a blank, such as the Natio l Bureau of Standards

10d (Bessemer steel) or 50a (chrome–tungsten–vanadium) be taken through all steps of the determination.

C. Determination of Cobalt in Plain Carbon and Other Steels Containing Less Than 0.10% Cobalt

"Dissolve a ten-gram sample in hydrochloric acid and cautiously oxidize with just enough nitric acid. Extract the iron with ether and wash the ether extract once with diluted hydrochloric acid. Warm the ether-extracted acid solution to expel residual ether, and oxidize with potassium chlorate. Dilute to 200 ml. and precipitate twice with zinc oxide," as described on page 211. "In material containing very little cobalt, it is advantageous to combine the extracted acid solution obtained in ether separations of a number of separate ten-gram samples."

Note on Ether Extraction. The hydrochloric acid solution containing iron is evaporated to a syrupy consistency, is taken up with hydrochloric acid (sp. gr. 1.1), and transferred by means of more of the acid to a separatory funnel. The cold acid solution is extracted several times by shaking with ether, cooling the mixture under the tap if necessary.

D. Determination of Cobalt in Cast Iron, Open-Hearth Iron, and Wrought Iron

Proceed as for plain carbon steels.

Various other methods for the determination of cobalt in steel, or in the presence of a large amount of iron, have been described.[5, 8, 9]

In principle these methods do not differ from the A. S. T. M. method already described, and for details the original papers should be consulted.

E. Determination of Cobalt in Magnet and High-Speed Tool Steel[10]

To a 1.00-g. sample add 20 ml. 8 *N* hydrochloric acid and heat until the steel has dissolved. Add 2–3 ml. 7.5 *N* nitric acid and boil gently for 3 minutes. Transfer the solution to a separatory funnel with the aid of 6 *N* hydrochloric acid, cool to 5°C., and shake with 50 ml. of

[8] A. Eder, *Chem. Ztg.* 46, 430 (1922).
[9] A. Craig and L. Culdroff, *Chemist-Analyst*, 24, 10 (1935); *Chem. Abstracts*, 30, 46 (1936).
[10] J. I. Hoffman, *J. Research Natl. Bur. Standards*, 8, 659 (1932).

ether. Allow to stand in cold water for 3 minutes and drain off the aqueous layer into another separatory funnel. Add 10 ml. 6 *N* hydrochloric acid to the ether solution and shake, eventually draining off the acid into the other funnel. To the entire aqueous solution add 50 ml. more of ether and repeat the above operations. Evaporate the aqueous solution, from which nearly all ferric chloride has been removed by the above treatment, nearly to dryness, add 15 ml. 5 *N* nitric acid and evaporate to dryness. Add 50 ml. 0.12 *N* hydrochloric acid and heat until all salts have dissolved. If more than 10% cobalt is present in the original sample, take an aliquot at this point. Pour the solution into 150 ml. 5% sodium hydroxide to which about 2 g. sodium peroxide has been added. Heat gently for 30 minutes to destroy excess peroxide and effect the complete precipitation of nickel and cobaltic hydroxide, along with manganese dioxide, etc. Cool, filter, and dissolve the washed precipitate in 15 ml. 5 *N* hydrochloric acid. Add to the solution 150 ml. water and neutralize to litmus with ammonium hydroxide. Cool to 10°C.; precipitate the remaining iron and copper with 10 ml. 6% cupferron solution. Filter, and wash the precipitate with a mixture prepared from 20 ml. cupferron solution and 1 liter cold 0.12 *N* hydrochloric acid. To the filtrate and washings, having a volume of about 400 ml., add 10 ml. or more of the solution prepared from 1 g. α-nitroso-β-naphthol in 15 ml. glacial acetic acid. Heat to 70° and, after 20 minutes, or longer, filter and wash the cobalt precipitate with hot 3 *N* hydrochloric acid. Dry, ignite, and weigh as Co_3O_4, which contains 73.42% cobalt. For greater accuracy, the precipitate should be ignited in hydrogen and weighed as cobalt.

The method has been successful in determining cobalt in low-cobalt steels, or in magnet steels containing 40% cobalt. When more than 0.2 g. of nickel and manganese is present, the zinc oxide separation is preferred, because the peroxide precipitate is too bulky.

F. Amperometric Titration of Cobalt[3]

The solution to be analyzed, free from interfering elements, should be 0.01 to 0.0005 *M* in cobalt (0.6 to 0.03 mg. per ml.), about 0.1 to 0.2 *M* in sodium acetate, and 0.1 *M* in acetic acid. After the solution is introduced into the titration cell, air is removed with nitrogen or hydrogen, and the cobalt is titrated with a standard solution (approximately 0.1 *M*) of α-nitroso-β-naphthol in 60% acetic acid at a potential of −0.6 v. (*vs.* the saturated calomel electrode) at the drop-

ping mercury electrode. The reagent is standardized in the same manner, using a solution of known cobalt content. Solutions of reagent that have been freed of suspended matter by filtration, and kept in dark bottles, retain their titer for at least 3 weeks. With amounts of cobalt varying between 1.5 and 12 mg. in 50 ml., the accuracy and precision are 0.5%. With smaller amounts, 0.59 and 0.29 mg. in the same volume, the accuracy is about 2%.

Copper and palladium can probably also be titrated amperometrically with the reagent.

II. Determination of Iron

A. Determination of Iron in the Presence of Aluminum[11] and Gallium[12]

The reagent has found some use in the gravimetric determination of ferric iron, and its separation from other elements, including aluminum and gallium. The solution containing up to 0.36 g. iron (as Fe_2O_3) as chloride or sulfate is neutralized with ammonia to the first appearance of a permanent precipitate. The precipitate is just dissolved with hydrochloric acid, and a volume of 50% acetic acid equal to the original volume of the solution is added. Iron is precipitated from the cold solution by slow addition of the reagent. After standing for several hours, the precipitate is filtered on ashless paper, washed with cold 50% acetic acid, and then with water. The precipitate and paper are dried, and then ignited to ferric oxide, Fe_2O_3, which contains 69.94% iron. Phosphates must be absent, for they contaminate the iron precipitate.

B. Determination of Iron in the Presence of Zirconium[13]

The solution should contain no more than 0.11 g. iron (as Fe_2O_3) and 0.30 g. zirconium (as ZrO_2) as chlorides in a total volume of 100–150 ml., and should be slightly acidic. To the solution is added 20 ml. oxalic acid solution (126 g. $H_2C_2O_4 \cdot 2\,H_2O$ per liter) and 5 ml. hydrochloric acid (sp. gr. 1.18). After stirring to dissolve the zirconium oxalate, 10 ml. glacial acetic acid is added; the solution is heated to boiling, and the iron is precipitated with α-nitroso-β-naphthol reagent. After standing for several hours, the precipitate is

[11] M. Ilinski and G. von Knorre, *Ber.*, **18**, 2728 (1885).
[12] J. Papish and L. C. Hoag, *J. Am. Chem. Soc.*, **50**, 2118 (1928).
[13] G. von Knorre, *Z. angew. Chem.*, **17**, 641, 676 (1904).

filtered on ashless paper, washed first with 50% acetic acid then with water, dried, and ignited to ferric oxide, Fe_2O_3.

III. Miscellaneous Determinations

Palladium. The separation of palladium from platinum and rhodium[14] and its separation from copper and iron[15] have been reported. Fair results are obtained, but the reagent offers no advantage over dimethylglyoxime for precipitating palladium (see page 154).

Copper.[16] The reagent is of limited value for the gravimetric determination of copper since the precipitate must be ignited; many others of greater selectivity and convenience of use are available.

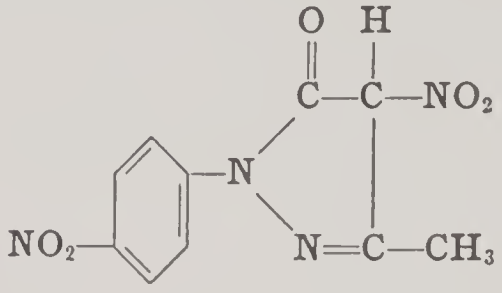
Potassium.[17] Potassium is determined indirectly by determining the cobalt in potassium cobaltinitrite precipitates using α-nitroso-β-naphthol. Such a method would seem to introduce an extra step, in that the precipitate would be analyzed gravimetrically for cobalt, and no advantage is apparent.

[14] W. Schmidt, *Z. anorg. Chem.*, **80**, 335 (1913).
[15] M. Wunder and V. Thuringer, *Z. anal. Chem.*, **52**, 737 (1913).
[16] R. Burgess, *Z. angew. Chem.*, **9**, 596 (1896).
[17] M. Delaville and P. Carlier, *Compt. rend.*, **182**, 701 (1926).

CHAPTER XIV

Picrolonic Acid

(1-*p*-Nitrophenyl-3-methyl-4-nitropyrazol-5-one)



Molecular weight: 264.2
Melting point: 125°C. (dec.)
Solubility: soluble in alcohol; moderately soluble in water
Reagent solution: 0.01 *M* in water, prepared by heating the calculated quantity of reagent in water and filtering the cooled solution; stable for considerable time

Some important uses of picrolonic acid in quantitative analysis have been found in the gravimetric and volumetric determinations of calcium, and in the gravimetric determination of lead. A method for the gravimetric determination of thorium has also been described which, when used on the micro scale, offers definite advantages. Since copper also forms a slightly soluble salt with the reagent, there is a possibility of determining that element with picrolonic acid, but no procedure has been developed. A number of other elements are also known to give insoluble picrolonates. These include magnesium, barium, strontium, iron, and manganese. Presumably other heavy metals and transition elements would form insoluble salts under the proper conditions, *i.e.*, in weakly acid or neutral solutions. The picrolonates form well-defined crystals, a fact that has been of value in qualitative analyses using picrolonic acid.[1]

Calcium picrolonate generally has the composition $Ca(C_{10}H_7N_4O_5)_2 \cdot 8\,H_2O$. If dried in air, the salt can be weighed directly. The calcium salt precipitates initially in a voluminous amorphous form,

[1] W. V. Eisenberg and G. L. Keenan, *J. Assoc. Official Agr. Chem.*, **27**, 177 (1944).

which upon digestion becomes crystalline; the crystals are a yellow-orange color. From dilute solutions, calcium picrolonate precipitates slowly as the crystalline form. The salt is soluble in acetic acid (probably other acids also), and precipitation is generally carried out at around *p*H 4–6. It has been reported[2] that the optimum *p*H for the precipitation of calcium picrolonate is 2–3, although the conditions are unstated. The solubility of the salt in water, at 18°C., *p*H unknown, has been given[3] as corresponding to 0.5 mg. calcium per 100 ml. (as compared with the solubility corresponding to 0.15 mg. calcium per 100 ml. from calcium oxalate under the same conditions). The presence of excess picrolonate ions reduces the solubility of the calcium salt in water, as shown in the following table. The investigators[3] do not claim high accuracy for these data.

Concentration of sodium picrolonate, g./liter	Solubility of $Ca(C_{10}H_7N_4O_5)_2 \cdot 8\ H_2O$, g./100 ml.
0.000	0.0168
0.100	0.0074
0.194	0.0054
0.200	0.0054
0.500	0.0038
1.000	0.0043

Determination of the solubility of calcium picrolonate by a polarographic method[4] gives a value corresponding to 9.6 mg. calcium ion dissolved per liter water at 20°C. and in a buffer of *p*H 3.6 to 3.8. This value is in agreement with a value of 9 mg. calcium ion per liter at 21°C., reported earlier, and obtained in the conventional method for determining solubility.[5] On the basis of insolubility alone, it might be concluded that calcium picrolonate as a precipitation form offers no advantage over calcium oxalate. The principal advantage is one of having a convenient weighing form, and a very favorable conversion factor (the precipitate contains 5.642% calcium).

Magnesium, barium, and strontium picrolonates are also insoluble; their molar solubilities are of the same order as the calcium salt,[3] although from the data they appear somewhat less in the cases of magnesium and strontium. Hence, extreme caution is warranted when determining calcium in the presence of unknown amounts of alkaline

[2] K. Tanii, H. Hosimiya, and T. Ikeda, *J. Chem. Soc. Japan*, **61**, 269 (1940); *Chem. Abstracts*, **34**, 4687 (1940).
[3] P. L. Robinson and W. E. Scott, *Z. anal. Chem.*, **88**, 417 (1932).
[4] G. Cohn and I. M. Kolthoff, *J. Biol. Chem.*, **147**, 705 (1943).
[5] R. Dworzak and W. Reich-Rohrwig, *Z. anal. Chem.*, **86**, 98 (1931).

earths. Presumably a tenfold excess of magnesium can be tolerated, with no danger of interference in the calcium determination.[5] The effect of the presence of other ions has not been investigated in a quantitative manner.

Lead is quantitatively precipitated from neutral solutions as the crystalline salt $Pb(C_{10}H_7N_4O_5)_2 \cdot 1.5\ H_2O$. The *p*H range for precipitation has been given as 2 to 6.5, although under unspecified conditions. The salt is somewhat more soluble at 0°C. in 0.1 *N* acetic or nitric acid than in water, but again the solubility in water is decreased by the presence of excess picrolonate ions.[6] The conversion factor, 0.2725, is rather favorable for an element as heavy as lead. The use of picrolonic acid to conclude the determination of lead in alloys (page 229) seems to offer certain advantages.

The thorium salt precipitates as $Th(C_{10}H_7N_4O_5)_4 \cdot H_2O$, containing 17.82% thorium, at *p*H 2 to 3.2.[2] Precipitation occurs from a boiling solution and the precipitate, which is colloidal, is rather difficult to filter. Thorium picrolonate is soluble in water, *p*H unknown, at 20°C. to the extent of 0.16 mg. per liter, and is somewhat more soluble in nitric and acetic acids.[7] The chief advantage gained from the use of picrolonic acid to determine thorium is the weighing form, both from point of convenience and favorable conversion factor. A direct separation of thorium from the rare earths cannot be made, although the reagent may be used to determine thorium following its preliminary separation as the hydrated peroxide.

I. Determination of Calcium

A. Gravimetric Determination of Calcium

The solution to be analyzed should contain no more than 0.1 g. calcium, and no more than a tenfold excess of magnesium. Alkali metals, as well as ammonium salts, may be present. The solution is neutralized to litmus, heated to about 50°C., and reagent solution is added slowly until a precipitate appears. If the precipitate is flocculent, it is stirred until it changes into the coarse crystalline form; then more reagent is added, with stirring if necessary to produce the crystalline precipitate. When precipitation is complete, a volume of picrolonic acid equal to about half the total volume of the solution

[6] F. Hecht, W. Reich-Rohrwig, and H. Brantner, *Z. anal. Chem.*, **95**, 152 (1933).
[7] F. Hecht and W. Ehrmann, *Z. anal. Chem.*, **100**, 87 (1935).

being analyzed is added, and the precipitate is allowed to stand for several hours or overnight.

The calcium picrolonate is filtered on a filtering crucible of medium porosity, which has previously been washed and dried to constant weight by drawing air through it on a filter pump, and then washed with two small portions of cold water. The precipitate is dried in the same manner; about 2 hours are required for constant weight to be attained. The air should be filtered through cotton or glass wool. The precipitate finally weighed contains 5.642% calcium.

The filtrate from the calcium precipitation may be used for the determination of magnesium (as magnesium ammonium phosphate or the pyrophosphate) if sufficient alcohol is added to make the total alcohol content of the solution about 20% by volume. Alcohol is necessary to prevent coprecipitation of ammonium picrolonate with the magnesium precipitate. The presence of the former substance is particularly undesirable, since upon ignition of magnesium ammonium phosphate the ammonium picrolonate will explode.

B. Polarographic Determination of Calcium[4]

Calcium picrolonate crystallizes slowly and is appreciably soluble in the absence of an excess of picrolonic acid; hence, an amperometric titration is not feasible. Instead, the determination is carried out by adding an excess of picrolonic acid, and measuring the amount left in solution. The approximate calcium content of the sample is first determined by a preliminary test. This consists in adding buffer and picrolonic acid to the solution of the sample, and noting the time required for the appearance of a precipitate of calcium picrolonate. Table XXII gives results that may be expected in this test. It is best

TABLE XXII

Time Required for Appearance of Calcium Picrolonate Precipitate[a]

Calcium ion, *M*	Time for appearance of precipitate
0.01	20–25 seconds
0.005	About 1 minute
0.003	About 1.5 minutes
0.002	About 2 minutes
0.001	2–3 minutes

[a] To 1 ml. calcium solution are added 0.3 ml. buffer and 2 ml. 0.01 *M* picrolonic acid.

to compare the unknown with standards, of approximately the same composition, tested in a similar manner. When the approximate concentration of the solution has been established, buffer solution (1 *M* acetic acid, 0.125 *M* lithium acetate, and 1 *M* lithium chloride) is added in such a quantity that it becomes about 10 times diluted in the final mixture. An amount of standard 0.01 *M* picrolonic acid is added to 5 to 10 ml. of the unknown solution so that the concentration of picrolonic acid after completed precipitation becomes at least 0.001 *M*. The amount of picrolonic acid added shall not exceed the fourfold molar concentration of the calcium. The mixtures are kept overnight in an ice box when the calcium concentration is equal to or smaller than 5×10^{-3} *M*. When the calcium concentration is greater, the solution is kept at room temperature (not above 20°). The residual concentration of picrolonic acid is determined, without filtering, polarographically at 20°C. at a cathode potential of −1.1 v. *vs.* the saturated calomel electrode, or at −1.2 v. applied potential when a mercury pool anode is used. The picrolonic acid solution is prepared from the solid acid, recrystallized from 33% acetic acid, and is standardized by titrating with carbonate-free 0.1 *M* sodium hydroxide, using phenolphthalein as the indicator.

The method is accurate within 1 to 2%. Results are good in the determination of 0.001 to 0.01 *M* calcium solutions, even when the concentrations of alkali, magnesium, sulfate, and phosphate ions are from 10 to 100 times larger than that of the calcium.

Another adaptation of the polarographic method for the determination of picrolonic acid, and thus indirectly calcium, has been made by Cohn and Kolthoff.[8] The method is an adaptation of one devised by Bolliger[9] in which picrolonic acid is titrated with methylene blue. The methylene blue picrolonate is extracted from the aqueous solution by chloroform; the end point is reached when the chloroform fails to remove the blue-green color formed in the aqueous solution upon the addition of titrant. The method for determining calcium was based on the precipitation of the element with excess of standard picrolonic acid, followed by titration of the excess with methylene blue. In the modified method the methylene blue titration of the residual picrolonic acid is carried out amperometrically.

The polarography of picrolonic acid has been described earlier (page

[8] G. Cohn and I. M. Kolthoff, *J. Biol. Chem.*, **148**, 711 (1943).
[9] A. Bolliger, *Proc. Roy. Soc. New South Wales*, **68**, 197 (1934); **69**, 68 (1935). *Australian J. Exptl. Biol. Med. Sci.*, **13**, 75 (1935).

221). Methylene blue is also reduced at the dropping mercury electrode. In a buffer composed of 0.1 *M* acetic acid, 0.0125 *M* lithium acetate, and 0.1 *M* lithium chloride, at 20°C., a single wave with a well-defined diffusion current appears at an applied potential of 0.3 v. (corresponding to a cathode potential of 0.2 v. *vs.* the saturated calomel electrode). The half-wave potential at this particular *p*H is −0.07 v. *vs.* the saturated calomel electrode. The diffusion current is proportional to the concentration of methylene blue, hence the amperometric titration of picrolonic acid with a solution of methylene blue is possible.

Amperometric Titration of Picrolonic Acid

To 10 ml. of 0.001 to 0.05 *M* picrolonic acid solution in the titration cell is added 1 ml. buffer solution which is 1 *M* in acetic acid, 0.125 *M* in lithium acetate, and 1 *M* in lithium chloride. Mercury is added to the cell to serve as anode. Oxygen is removed by passing nitrogen or hydrogen through the solution for 10–15 minutes. The picrolonic acid is titrated amperometrically at room temperature at an applied e.m.f. of 0.3 v. with 0.01 *M* methylene blue chloride solution, which is added from a microburet. After each addition of methylene blue, hydrogen or nitrogen is passed through the liquid for 1 minute in order to stir the mixture and to remove oxygen. The end point is found graphically, a correction for dilution being made. The methylene blue solution is standardized in the same way with picrolonic acid of known strength. The strength of the picrolonic acid solution is determined by titration with standard sodium hydroxide, phenolphthalein being used as the indicator (see page 221).

For use of this method in the determination of calcium, the calcium is first precipitated with excess of standard picrolonic acid, as already described. After complete precipitation the cooled mixture is filtered through a Jena G4 sintered glass crucible; the filtrate is brought to room temperature, and an aliquot is used for titration.

From the practical point of view the direct polarographic method is to be preferred, since no filtration is required and the diffusion current of the residual picrolonic acid may be determined directly.

C. Microdetermination of Calcium

Three distinctly different micro methods for the determination of calcium, in addition to the polarographic methods described in the

preceding section, are worthy of mention. These include a conventional micrograviметric method, a microvolumetric method, and a microgasometric method.

1. Micrograviметric Method

Except for manipulative details, this method follows rather closely the procedure given for determining larger amounts of calcium. A micro filter beaker, in which both precipitation and weighing of the calcium picrolonate can be carried out, should be employed. Weighings should be made using another micro filter beaker as a tare. The sample in the form of a solution is introduced by means of a pipet; the weight of the solution may be determined after capping the beaker to avoid errors due to evaporation during the weighing. Precipitation is carried out as in the macro method, and the solution is allowed to stand for at least an hour at 0°C. before filtering. The precipitate is washed with 2 0.2-ml. portions of water. To dry the precipitate, the neck of the filter beaker is closed with a Pregl dust filter; the filter support is brought into a vertical position and the air stream is aspirated through the container for about half an hour. The outside of the container is cleaned, and after standing for 10 minutes on the microbalance the precipitate is weighed.

2. Microvolumetric Method (Titration with Methylene Blue)

The principle of this method has already been described (page 221). The method has been studied critically by Cohn and Kolthoff.[8] The procedure recommended is essentially the same as that of Bolliger. To 20–30 ml. chloroform (or methylene dichloride) in a separatory funnel 2–10 ml. of 0.001 to 0.005 *M* picrolonic acid and 2 ml. of an acetate or phosphate buffer of between *p*H 4 and 8 are added. The picrolonic acid is titrated with 0.001 *M* methylene blue chloride, the end point being reached when the blue-green color formed in the solution upon the addition of methylene blue is no longer extractable by chloroform. After a rough preliminary titration to determine the approximate strength of the picrolonic acid, a second titration is carried out in which the amount of methylene blue added is about 1 to 2 ml. smaller than the total amount required. The methylene blue picrolonate is extracted with 20-ml. portions of chloroform (or less, if ethylene dichloride is used) until the freshly added chloroform remains colorless. The titration is finished by adding each time about 0.15

ml. methylene blue solution and extracting the blue-green product from the aqueous solution with 20-ml. portions of chloroform (two are usually sufficient). The end point is reached when the chloroform fails to remove the color from the aqueous solution. The methylene blue may be standardized in the same manner with a picrolonic acid solution standardized previously with sodium hydroxide.

In the determination of calcium using this titration, the precipitation is carried out according to directions already given (page 219). After precipitation the mixture is filtered through a fine porosity filtering crucible (paper is not permissible, as it absorbs picrolonic acid). The filtrate is brought to room temperature, and an aliquot is used for the titration. For amounts of calcium ranging from 1 to 10 mg. a maximum error of 3% has been shown.

3. Microgasometric Method[10–12]

The development of a rapid and accurate gasometric procedure for the microdetermination of organic carbon makes possible the indirect determination of rather small quantities of calcium. The method is based on the precipitation of calcium as picrolonate, followed by wet combustion of the precipitate and measurement of the volume of carbon dioxide produced.

The wet combustion method, developed to a high degree of usefulness by Van Slyke and co-workers, employs an oxidizing mixture consisting of chromic, iodic, sulfuric, and phosphoric acids. The organic material to be analyzed is converted to carbon dioxide and other products upon heating with the oxidizing mixture; the carbon dioxide is absorbed in a solution of sodium hydroxide containing hydrazine to reduce any free halogens that may have been liberated during the oxidation. Other gases, including oxygen and nitrogen, are expelled from the system; the carbon dioxide is liberated from the alkali with acid, and its pressure is measured at some constant volume, either 2 or 10 cc.

The method may be employed on substances containing nitrogen, sulfur, halogens, and the alkali metals, without interference; as little as 0.1 mg. carbon may be determined. The upper limit for a determination is about 15 mg. carbon. In terms of calcium, since calcium picrolonate contains 20 atoms carbon per atom calcium, the lower

[10] D. D. Van Slyke, I. H. Page, and E. Kirk, *J. Biol. Chem.*, **102**, 635 (1933).
[11] D. D. Van Slyke, J. Folch, and J. Plazin, *ibid.*, **136**, 509 (1940).
[12] D. D. Van Slyke and F. J. Kreysa, *ibid.*, **142**, 765 (1942).

limit for a determination is about 20 μg. The error in determining amounts of carbon less than 1 mg. is of the order of 0.5%; the error is 0.2% when handling amounts of carbon ranging up to 15 mg.

Apparatus Required. For the gasometric determination of carbon in the calcium picrolonate precipitates the Van Slyke-Neill manometric apparatus, modified according to Van Slyke and Folch, is used. This equipment may be purchased from laboratory supply houses, and since the manner of its operation is highly detailed, reference should be made to the original literature for operating directions.

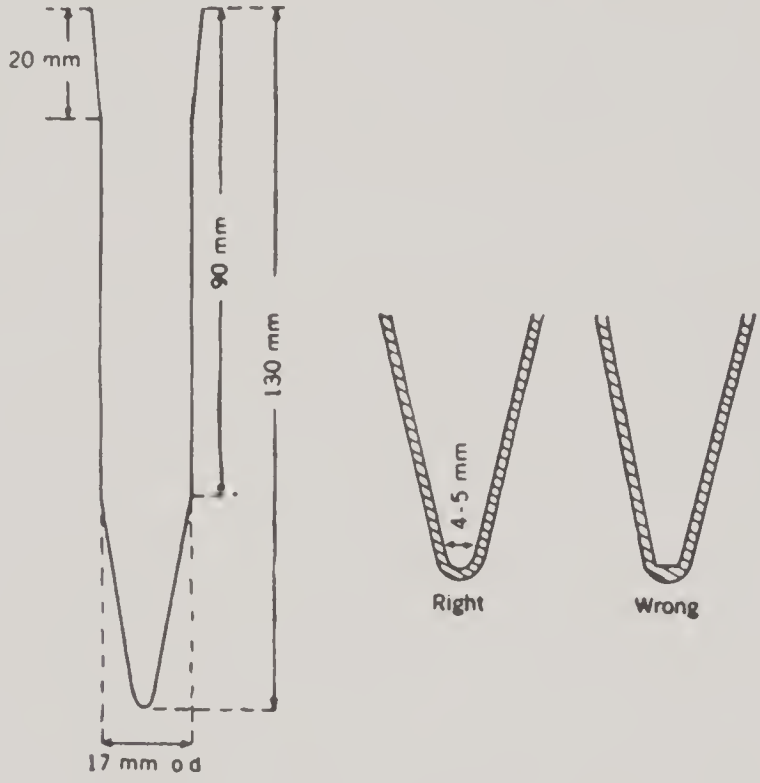


Fig. 11. Combustion-centrifuge tubes.

The manometric apparatus is modified only slightly for the determination of calcium; the combustion tube conventionally used on the apparatus is tapered into a cone at the bottom, so that it can serve also as a centrifuge tube (see Fig. 11). The bottom of the tube must have the dimensions and shape shown in order to hold the precipitates and to permit complete decantation of the supernatant liquid.

Other apparatus required in connection with the analysis includes a drying oven, muffle furnace, and stirring rods about 2 mm. in diameter. The combustion-centrifuge tubes and the stirring rods are cleaned in chromic acid cleaning mixture, heated to 120–140°C., and

then rinsed with distilled water. They are stored in a desiccator over phosphorus pentoxide (calcium must be avoided), or the washed tubes and rods may be inverted in a covered beaker or wide-mouth Erlenmeyer flask and dried in the oven.

Reagents Required. For the precipitation of calcium, a solution of picrolonic acid approximately 0.008 *M* should be prepared. Only the recrystallized acid should be used in making this solution. To prepare the solution 2.1 g. picrolonic acid and 1 liter water are placed in an Erlenmeyer flask covered with a watch glass to retard evaporation and heated for 2–3 hours on a steam bath, and are shaken occasionally. The solution is cooled to room temperature and filtered through a calcium-free filter paper to remove any undissolved residue. The solution is kept in an ice box so that any material that is insoluble at 0°C. will precipitate before the solution is used. Hydrochloric acid, approximately 0.04 *M*, is required, as is a dropping bottle of concentrated sulfuric acid.

The combustion mixture is prepared as follows: in a 1-liter Pyrex Erlenmeyer flask, provided with a ground-glass stopper, is placed 25 g. chromium trioxide. To this is added 167 ml. of syrupy phosphoric acid (sp. gr. 1.7), followed by 333 ml. fuming sulfuric acid (containing 20% free sulfur trixiode). With the stopper left off, the mixture is heated to 140–150°, the flask being gently rotated from time to time. When a temperature of 150° has been reached, the flame is removed and the flask is covered with an inverted lipless 150-ml. beaker; the mixture is allowed to cool to room temperature. The flask is stoppered when cool, and the inverted beaker is kept permanently over the stopper as a precaution against contamination. The solution should not be allowed to absorb moisture. Iodic acid is added, in the form of potassium iodate, immediately before making a determination.

Procedure. A sample containing 20 to 120 μg. calcium is measured into the combustion–centrifuge tube and concentrated to dryness by placing the tube in the oven at 100–105°. If any organic matter is present, it is then destroyed by adding a drop of concentrated sulfuric acid and ashing at 480–520°C. in the muffle.

To dissolve the ash, 1 ml. 0.04 *M* hydrochloric acid is added. A clean stirring rod is used to loosen up the ash, and is left in the tube while the latter is immersed in boiling water for 10 minutes. Then 1 ml. hot distilled water is added and the heating is continued for an-

other 10 minutes to complete solution of the ash. The solution is cooled to room temperature and 2 ml. ice-cold picrolonic acid reagent is added. The liquids are stirred occasionally with the rod until crystals of calcium picrolonate appear, which occurs in 3–5 minutes. After 0.5 hour at room temperature, the tube is cooled to almost 0° by immersion in ice water, and is kept at this temperature for 1.5 hour. During the first 0.5 hour it is stirred 2 or 3 times. The stirring rod is then withdrawn and rinsed into the tube with 1 ml. picrolonic acid solution. The tube is capped and left for 1 hour longer at 0° to complete the crystallization.

The tube is then centrifuged for 15 minutes at 3000 r.p.m. and the supernatant fluid is removed by suction through a fine curved capillary. To avoid loss of any of the crystals floating on the surface film, suction is not started until the capillary is immersed well below the surface. Then as the fluid is withdrawn the particles in the surface film adhere to the walls of the centrifuge tube and are not lost. Suction is stopped when 0.2–0.3 ml. of fluid remains over the precipitate.

To drain off the remainder of the solution the tube is inverted to an angle of about 30° with the horizontal and the lip is rested on a wet towel or filter paper. If a drop of liquid adheres in the narrow bottom of the tube, it is touched with a curved platinum wire, which breaks the surface film and starts drainage. After 2 minutes at the 30° angle the tube is shifted to a nearly vertical position and left there for 15 minutes to complete the drainage. The mouth of the inverted tube is sprayed with a few drops of water to remove adherent picrolonic acid solution from the lip. Drainage in this manner leaves in the tube a uniform film of approximately 0.025 ml. of liquid. This film contains 0.031 mg. of picrolonic acid, equivalent to 2.3 μg. calcium. Variations in the film are not great enough to cause variations of more than $\pm$ 1 mm. in the blank, equivalent to 0.2 μg. calcium.

After the tube has drained, the carbon in the precipitate is determined by the combustion method described by Van Slyke and Folch, the centrifuge tube serving as combustion tube. The pressure readings are made with the gases at 2 cc. volume.

A blank analysis is run by placing 3 ml. picrolonic acid solution and 2 ml. water in the centrifuge–combustion tube, after the latter has been properly cleaned. The picrolonic acid solution is decanted; the tube is drained exactly as in the analysis, and is subjected to combus-

tion. The value of $p_1 - p_2$ (p_1 and p_2 are manometer readings before and after the absorption of carbon dioxide), measured with the gas volume at 2 cc., obtained in this blank combustion is the correction, c. It includes a correction of about 10 mm. for the carbon in the picrolonic acid of the film left in the tube after draining.

Calculation of Results. The micrograms of calcium in the sample are calculated by multiplying the carbon dioxide pressure, P_{CO_2}, from the burned precipitate by a factor given in Table XXIII (which are

TABLE XXIII

Factors for Calcium Calculation

Temperature, °C.	Factor; μg. Ca indicated by 1 mm. P_{CO_2}, at 2.000 cc.[a]
10	0.2460
11	0.2446
12	0.2433
13	0.2421
14	0.2409
15	0.2398
16	0.2386
17	0.2376
18	0.2364
19	0.2353
20	0.2341
21	0.2331
22	0.2319
23	0.2309
24	0.2299
25	0.2289
26	0.2279
27	0.2269
28	0.2259
29	0.2251
30	0.2241
31	0.2231
32	0.2223
33	0.2214
34	0.2204
35	0.2196

[a] If the volume is not exactly 2.000 cc., multiply the factor in the table by volume/2.

factors for milligrams of carbon multiplied by 1000 × 0.16686, the ratio of the weights of 1 calcium atom to 20 carbon atoms):

$$\mu g.\ \text{Ca} = P_{CO_2} \times \text{factor}$$

$$P_{CO_2} = (p_1 - p_2 - c)$$

where p_1 and p_2 are manometer readings before and after absorption of the carbon dioxide, and c is the blank, obtained above.

The method has been used on blood serum and on tap water, as well as on relatively pure calcium samples. In the latter analyses, errors of a few tenths of a per cent are reported for calcium in amounts ranging from 40 to 100 μg.; on 20-μg. samples the error may be as large as 1.5%. Results obtained on serum samples compare well with those obtained in the calcium oxalate–permanganate microtitration, and recovery of added calcium to serum samples is within a few per cent of the expected value at the 40–50 μg. level.

This method, while not as simple as some others, appears to offer definite advantages in the determination of microgram quantities of calcium, and could easily be put into use in laboratories already in possession of the manometric apparatus.

II. Determination of Lead

The solution to be analyzed should contain no more than 0.10 g. lead in 50 ml., only traces of alkali metal or ammonium salts, and should be neutral to litmus. Picrolonic acid is added slowly with stirring to the boiling solution, a total volume of 150 ml. of the 0.01 *M* reagent being used. After being cooled to 0°C., the precipitate is filtered on a filtering crucible of medium porosity, washed with 50 ml. cold water, and dried to constant weight at 130–140°C. The precipitate contains 27.25% lead. A microgravimetric method, using essentially the same procedure as given, has been described.[6]

Determination of Lead in the Presence of Metals[13]

Not more than 0.100 g. lead may be determined in the presence of aluminum, antimony, arsenic, barium, bismuth, cadmium, chromium, cobalt, copper, iron, manganese, mercury, nickel, silver, and zinc. Thallium interferes and must be absent.

The solution to be analyzed should be as small in volume as pos-

[13] C. Mahr and H. Ohle, *Z. anorg. Chem.*, **234**, 224 (1937).

sible (50–100 ml.) and should be 1–2 *N* in nitric acid. An equal volume of thiourea solution, about 30% saturated and in 1 *N* nitric acid, is added. If preferred, solid thiourea may be added to the unknown until about 30% saturated. The solution is cooled in an ice bath to almost 0°C., whereupon white crystals of 2 $Pb(NO_3)_2 \cdot 11\ CS(NH_2)_2$ separate. More solid thiourea is added to insure saturation of the solution at 0°, and to complex all interfering ions. After 30 minutes to 1 hour the precipitate is filtered and washed with 1 *N* nitric acid, saturated with thiourea, and chilled to 0°C. The precipitate is dissolved in hot water, and the lead is determined as described previously.

If an antimony- or tin-base alloy is to be analyzed for lead, the following procedure is employed. An amount of the alloy estimated to contain no more than 0.1 g. lead is dissolved in the minimum quantity of aqua regia. The solution is diluted to 75–100 ml., and 5–8 g. thiourea is added. After the thiourea has dissolved, the solution is cooled to 0° and the lead is precipitated. The determination is concluded as above. If much bismuth is present, the lead thiourea precipitate will be yellow in color. Under these circumstances, reprecipitation of the lead is recommended.

III. Determination of Thorium[7]

The solution should contain no more than 0.10 g. thorium, no alkali metal or ammonium salts, and no free nitric acid. Acetic acid sufficient to give a concentration of 2–3% by volume at the end of the precipitation is used. The solution, which should initially contain about 10 mg. thorium per 5 ml., plus acetic acid, is heated to boiling, and the picrolonic acid solution is added slowly with stirring. The total amount of reagent added should be 50 ml. per 10 mg. thorium. When all the reagent has been added the solution is allowed to cool at about 0–5°C. for 1 hour, then filtered through a filtering crucible of medium porosity. The precipitate is washed with 3 or 4 small portions of cold water, and air-dried to constant weight (see under calcium, page 220). The precipitate contains 17.82% thorium.

Microdetermination of Thorium[7]

Precipitation of thorium on the micro scale is best done in a filter beaker. However, because of the limited capacity of the beaker, some of the original solution must be evaporated to allow addition of suf-

ficient picrolonic acid solution. The method is somewhat slow, but the originators of the method claim a high degree of precision.

A microburet, graduated to permit estimation to the nearest 0.001 ml. is filled with the thorium solution. From this buret the solution is delivered to a previously dried and weighed filter beaker. The amount of solution added should be sufficient to contain several milligrams of thorium. The filter beaker is dried by drawing through it dust-free air.

The filter beaker containing the solution is heated to about 85°C. and dust-free air is drawn through to evaporate the solution. The air stream should be sufficiently gentle to prevent spattering of the solution in the beaker. The dry residue is dissolved in about 1 ml. hot water and enough glacial acetic acid is added by means of a micropipet so that the final acid concentration (before filtering the precipitate) will be about 3% by volume. The filter beaker is now heated gently to boiling, care being taken to prevent boiling over. To this solution is added 1.5 to 2 ml. picrolonic acid reagent in portions of 0.5 ml. and the solution is shaken carefully after each addition and heated on the hot plate until the boiling point is again reached. About 2.5 ml. picrolonic acid is required when the quantity of thorium exceeds 1 mg. When addition of the precipitant is complete the beaker is kept boiling gently, with occasional removal and shaking. When the precipitate has become crystalline and the supernatant liquid clear, additional picrolonic acid is pipetted in, to give altogether about 2.5 times the required quantity. If the volume totals more than 4–5 ml. (depending on the capacity of the beaker), no further reagent is added until after some of the solution is evaporated as described initially. If picrolonic acid crystallizes out, care should be taken to redissolve it by heating the solution over a boiling water bath. A preliminary determination is usually necessary before an accurate result can be obtained.

To calculate the volume of precipitant necessary, or to calculate the volume of precipitant that should be added after adding the first portion of picrolonic acid, the following procedure is carried out: 1 ml. 0.01 *N* picrolonic acid contains sufficient acid to precipitate 0.4 mg. thorium. The volume of liquid in the filter beaker can be estimated easily on the basis of its weight; now, if the capacity of the beaker is known, it is possible to judge the total amount of picrolonic acid necessary for precipitation, and how much should be evaporated in order to

have the final concentration of picrolonic acid in the solution about 50%.

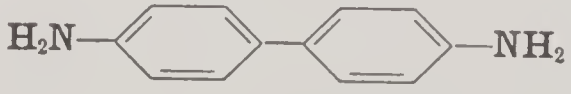
The determination is concluded as in the macro determination, after the supernatant liquid is removed and the precipitate is washed in the filter beaker.

CHAPTER XV

Precipitants for Anions

While the greatest number of organic precipitants described in this book are for cations, a few reagents have been developed which have proved of value in the precipitation and determination of anions. These include: benzidine, for the determination of sulfate and tungstate; nitron, for the determination of nitrate and perrhenate; tetraphenylarsonium chloride, for the determination of mercury, periodate, permanganate, perrhenate, tin, and other ions; and triphenyltin chloride for the determination of fluoride.

I. Benzidine



Molecular weight: 184.2
Melting point: variously given: 117°, 121°, 125°, 129°C.
Solubility: soluble in alcohol, ether; slightly soluble in water; hydrochloride soluble in water
Reagent solution: prepared by shaking 8 g. benzidine hydrochloride with 1 liter water and filtering; should be prepared weekly

Many reactions of benzidine with inorganic ions have been described. These might be classified broadly as: (*1*) reactions in which benzidine is oxidized to a colored substance and (*2*) reactions in which a normal or complex salt of benzidine is precipitated.

The many spot tests and colorimetric methods for detecting and determining oxidizing ions are included in the first category.[1] The reactions of immediate interest, such as the precipitation of sulfate and tungstate, are of the second type. Metallic ions, including cadmium, copper, silver, and zinc, form complex salts with benzidine that may be precipitated more or less completely with thiocyanate, etc. Copper, for example, may be precipitated and determined as insoluble Cu-

[1] For a detailed list of these reactions, see J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*. Wiley, New York. 1941, p. 214.

$(C_{12}H_{12}N_2)(SCN)_2$.[1a] The use of this type of complex usually presents no advantage over the conventional type of chelate complex, and a detailed consideration of them will not be given here.

A. Determination of Sulfate

Sulfate is precipitated as benzidine sulfate, $C_{12}H_{12}N_2 \cdot H_2SO_4$, by an aqueous solution of benzidine hydrochloride from slightly acid solutions which are free from oxidizing agents but which may contain divalent cobalt, copper, iron, manganese, nickel, zinc, and trivalent aluminum and chromium.[2] The solubility of the precipitate has been determined in water,[3] and in hydrochloric acid.[4] The results, shown in Tables XXIV and XXV, indicate that precipitation should be made

TABLE XXIV[a]

Solubility of Benzidine Sulfate in Water

Temperature, °C.	Average solubility, g./liter
0	0.049
25	0.097
50	0.145
80	0.271

[a] C. S. Bisson and A. W. Christie, *J. Ind. Eng. Chem.*, **12**, 485 (1920).

in the cold from weakly acidic solutions for minimum errors. Likewise, solubility losses will be less serious if large quantities (100 mg. or more) of sulfate are precipitated.[5]

The classical method of precipitation of sulfate by barium chloride affords a much more complete precipitation, but is subject to other well-known sources of error. The benzidine method offers the advantage of greater speed, since the precipitate may be titrated with alkali,[6–11] or with permanganate.[12]

[1a] P. Horkheimer, *Pharm. Ztg.*, **80**, 660 (1935).
[2] G. von Knorre, *Z. anal. Chem.*, **49**, 461 (1910).
[3] C. S. Bisson and A. W. Christie, *J. Ind. Eng. Chem.*, **12**, 485 (1920).
[4] W. B. Meldrum and I. G. Newlin, *Ind. Eng. Chem., Anal. Ed.*, **1**, 231 (1929).
[5] L. W. Haase, *Z. angew. Chem.*, **40**, 595 (1927).
[6] W. Müller, *Ber.*, **35**, 1587 (1902).
[7] W. Müller and K. Durkes, *Z. anal. Chem.*, **42**, 477 (1903).
[8] F. Raschig, *Z. angew. Chem.*, **16**, 617, 818 (1903).
[9] O. Huber, *Chem. Ztg.*, **29**, 1227 (1905).
[10] J. Biehringer and W. Borsum, *ibid.*, **30**, 721 (1906).
[11] C. Friedheim and O. Nydegger, *Z. angew. Chem.*, **20**, 9 (1907).
[12] P. L. Hibbard, *Soil Sci.*, **8**, 61 (1919).

TABLE XXV[a]

Solubility of Benzidine Sulfate in Hydrochloric Acid at 25°C.

Normality of acid	Solubility, g./1000 g. solution
0.000	0.098
0.239	0.542
0.530	0.942
1.009	1.254
2.074	1.790
2.825	1.930
4.139	1.887
5.622	1.774
7.601	1.544
9.942	1.499
11.099	1.490

[a] W. B. Meldrum and I. G. Newlin, *Ind. Eng. Chem., Anal. Ed.*, **1**, 231 (1929).

The sulfate solution is diluted so that the concentration of sulfate is 0.1 g. per 50 ml. or more of solution. For each mole sulfate no more than 10 moles hydrochloric acid, 15 moles nitric acid, 20 moles acetic acid, 5 moles alkali salt, or 2 moles ferric iron should be present.[13] An equal volume of the reagent is stirred in, and the precipitate is allowed to stand in ice water for 15 to 30 minutes. The *p*H of the solution should be about 3. The precipitate is collected on paper, using suction. Portions of the clear filtrate are used to transfer the last traces of precipitate, and the benzidine sulfate is washed with 80% alcohol, or with a saturated benzidine sulfate solution. The filter and precipitate are transferred to an Erlenmeyer flask; 50–100 ml. water is added, and the mixture is shaken. Several drops of phenolphthalein are added; the mixture is heated to about 50°C., and titrated with 0.1 *N* sodium hydroxide. Near the end point the solution is boiled for 5 minutes, and the titration is completed. One milliliter 0.1000 *N* sodium hydroxide is equivalent to 4.904 mg. sulfuric acid, or 4.80 mg. sulfate.

Methods for the determination of sulfur or sulfate in the following classes of materials have been described: blood serum and plasma,[14–21]

[13] C. Friedheim and O. Nydegger, *Z. anal. Chem.*, **49**, 464 (1910).
[14] H. L. White, *Am. J. Physiol.*, **65**, 537 (1923).
[15] R. S. Hubbard, *J. Biol. Chem.*, **88**, 663 (1930).
[16] C. L. Cope, *Biochem. J.*, **25**, 1183 (1931).
[17] D. P. Cuthbertson and S. L. Tompsett, *ibid.*, **25**, 1237 (1931).
[18] A. Lesure and A. Thomas, *J. pharm. chim.*, **17**, 114 (1933).
[19] W. S. Hoffman and R. Cardon, *J. Biol. Chem.*, **109**, 717 (1935).
[20] N. C. Das Gupta, *Ind. J. Vet. Sci.*, **8**, 119 (1938).
[21] M. H. Power and E. G. Wakefield, *J. Biol. Chem.*, **123**, 665 (1938).

minerals and technical products,[22–25] water,[26] soil extracts,[27] urine,[28–36] and wine.[37]

1. Microdetermination of Sulfate

Various procedures have been described for the microdetermination of sulfate by the benzidine method.[38–42] After precipitation the sulfate may be titrated with dilute barium chloride solution, using sodium rhodizonate as the indicator, or with dilute alkali. In another method the precipitated benzidine sulfate is oxidized with an excess of standard potassium permanganate solution, followed by titration of the excess with standard oxalate. The latter method has been carefully studied, and adapted to the determination of quantities of sulfate as low as 0.05 mg. with an error not exceeding 5%.[42]

The oxidation of the benzidine in the precipitate of benzidine sulfate is apparently nonstoichiometric; hence, the benzidine sulfate titer of the permanganate solution must first be determined. This would be less of a source of inconvenience in making a series of determinations than in making a single analysis, but nevertheless does detract somewhat from interest in the method.

The procedure, originally designed for the analysis of soil solutions, is adaptable to the analysis of many other types of sulfate-containing materials. A quantity of solution estimated to contain from 50 to 200 mg. of sulfate is pipetted into a small Pyrex beaker, 0.5 ml. nitric acid

[22] G. von Knorre, *Chem. Ind.*, **28**, 2 (1905).
[23] F. Raschig, *Z. angew. Chem.*, **19**, 331 (1906).
[24] M. L. Chepelevetzkii and S. I. Pozdnyakova, *J. Chem. Ind. U.S.S.R.*, **8**, 42 (1931); *Chem. Abstracts*, **26**, 1542 (1932).
[25] V. and M. Matula, *Chem. Ztg.*, **50**, 486 (1926).
[26] F. Raschig, *Z. angew. Chem.*, **19**, 334 (1906).
[27] A. W. Christie and J. C. Martin, *Soil Sci.*, **4**, 477 (1917).
[28] R. Gauvin and V. Skarzynski, *Bull. soc. chim.*, **13**, 1121 (1913).
[29] O. Rosenheim and J. C. Drummond, *Biochem. J.*, **8**, 143 (1914).
[30] G. W. Raiziss and H. Dubin, *J. Biol. Chem.*, **18**, 297 (1914).
[31] J. C. Dummond, *Biochem. J.*, **9**, 492 (1915).
[32] C. H. Fiske, *J. Biol. Chem.*, **47**, 59 (1921).
[33] S. Yoshimatsu, *Tôhoku J. Exptl. Med.*, **7**, 119 (1926); *Chem. Abstracts*, **20**, 2515 (1926).
[34] A. Friedrich, and E. Bauer *Z. physiol. Chem.*, **228**, 61 (1934).
[35] A. Friedrich and F. Mandl, *ibid.*, **235**, 174 (1935).
[36] E. C. Owen, *Biochem. J.*, **30**, 352 (1936).
[37] E. Lobstein and M. Ancel, *Ann. chim. anal. appl.*, **15**, 389 (1933).
[38] G. Zimmerlund and O. Svanberg, *Svensk. Kem. Tid.*, **34**, 139 (1922); *Chem. Abstracts*, **17**, 703 (1923).
[39] M. Chatron, *Bull. soc. chim. biol.*, **13**, 300 (1931).
[40] E. Ollgaard, *Biochem. Z.*, **274**, 181 (1934).
[41] M. H. Power, E. G. Wakefield, and R. D. Peterson, *J. Biol. Chem.*, **105**, 67 (1934).
[42] A. W. Marsden and A. G. Pollard, *J. Soc. Chem. Ind.*, **56**, 464T (1937).

(sp. gr. 1.42) is added, and the solution is carefully evaporated to dryness. The residue is moistened with a few drops of nitric acid and again evaporated to dryness. If it is necessary to destroy organic matter the beaker is placed in an oven at 400°C. for about 1 hour. When cool, the residue is moistened with a few drops of nitric acid and is again evaporated; after addition of a few drops of hydrochloric acid, a final evaporation to remove nitrates is made. The dry residue is taken up in 2 ml. water containing one drop 0.1 *N* hydrochloric acid. The mixture is warmed until a clear solution is obtained; it is then transferred to a pointed centrifuge tube, having an 8-ml. capacity, and graduated at 4 and 5 ml. The beaker is rinsed with 3 0.5-ml. portions of water and the contents of the tube are made up to 4 ml. The *p*H of the solution should be about 3, which is optimum for the precipitation of benzidine sulfate. To the solution in the tube is added 1 ml. benzidine hydrochloride reagent, and 5 minutes later the tube is placed in an ice–water mixture for 10 minutes. The tube is then centrifuged for 5 minutes at 3000 r.p.m.; the supernatant liquid is carefully decanted, and the tube is washed with 5 ml. 80% alcohol, the precipitate being stirred up with a thin glass rod. The tube is centrifuged as before, and the decantation and washing procedures are repeated. The tube is then placed in a beaker of hot water to evaporate the remaining traces of alcohol, 5 ml. of 0.5% potassium hydroxide are added, and when the precipitate has dissolved the contents of the tube are transferred to a 100-ml. Erlenmeyer flask. The tube is rinsed with four 5-ml. portions of water, the rinsings being added to the main solution in the flask. To the solution in the flask is added 1 ml. sulfuric acid (sp. gr. 1.8).

The solution thus obtained is heated to 60–70° on a steam bath, and the standard permanganate solution (0.05 *N*) is run in until the apparent end point is reached. A 25% excess of permanganate solution, plus 1 ml., is added, and the flask is heated for an additional 10 minutes. To the mixture is added 2.00 ml. 0.05 *N* sodium oxalate solution, and when reaction is complete the excess oxalate is titrated with permanganate. The net consumption of permanganate, in ml., multiplied by the factor for converting volume of permanganate into mg. sulfate, gives mg. sulfate. The original investigators found the factor to be 0.118.

The method, as used on soil solutions, has been found to give results agreeing within 5% with those obtained by the conventional barium

sulfate method. The concentration levels were from 200 to 800 p.p.m. sulfate, and analyses by the benzidine method were made on 1-ml. portions.

2. Manometric Combustion Method

Benzidine sulfate precipitates may also be analyzed by the manometric method—measuring the volume of carbon dioxide obtained upon wet oxidation of the precipitate.[43] By this method quantities of sulfur (as sulfate) in the range from 0.07 to 0.16 mg. can be determined with an average error of 0.5%, and it is possible to determine as little as 0.02 mg. without greatly increasing the error. The determination requires the Van Slyke-Folch apparatus for wet combustion, adapted for use with a centrifuge–combustion tube. Description of the apparatus is given in somewhat greater detail on page 224.

The sample to be analyzed may be blood or urine filtrates, or any other solution free from substances such as phosphate that would precipitate with benzidine. It should contain from 0.02 to 0.16 mg. sulfate (calculated as sulfur) in 2 ml. if the submicrocombustion is to be used, or 0.4 to 0.8 mg. if the microcombustion is to follow.

Details of the preparation of blood and urine filtrates have been given by Hoffman and Cardon,[19] and by Fiske.[32]

Procedure. To 2 ml. protein and phosphate-free solution are added 1 ml. acetone, followed by 1 ml. benzidine hydrochloride reagent (4 g. benzidine hydrochloride made up to 250 ml. with 0.2 *N* hydrochloric acid), added dropwise. As a check on reagents, control tubes are set up, with water in place of the filtrate. The control serves for a blank analysis which gives a correction covering all the reagents. The combustion tubes, covered to prevent contamination by dust, are set in the ice box for complete precipitation. A precipitate begins to form at once, and the reaction is complete in one hour.

The material is centrifuged for five minutes at 2000 r.p.m.; after this time the precipitate is packed tightly within the capillary portion of the tube. The supernatant fluid is decanted completely, and the tube is allowed to drain for 10 minutes in a rack on a lint-free towel. Four milliliters 90% acetone is added to each tube—the inside of the tube, including the ground-glass connection area, is washed down completely. The precipitate is not disturbed; mixing of the precipitate with acetone during washing is entirely unnecessary. The tube, after another 5 minutes of centrifugation and another decantation of super-

[43] C. L. Hoagland, *J. Biol. Chem.*, **136**, 543 (1940).

natant liquid, is drained as before. This procedure is repeated once more; then the tubes are placed in a boiling water bath for 30 minutes to remove all traces of acetone. The material is now ready for combustion, which is carried out in the manner described by Van Slyke and Folch.[44] A blank analysis, in which water replaces the sulfate solution, is also carried out.

TABLE XXVI

Factors for Calculation of Sulfur from P_{CO_2} Obtained by Combustion of Benzidine Sulfate Precipitate

Temperature, °C.	Factors to give mg. S	
	Submicroanalysis[a]	Microanalysis[b]
10	0.0003279	0.001624
11	61	16
12	44	08
13	28	00
14	12	0.001592
15	0.0003197	85
16	82	77
17	67	69
18	52	62
19	37	57
20	21	47
21	07	40
22	0.0003093	33
23	79	26
24	65	19
25	51	12
26	38	05
27	25	0.001499
28	12	93
29	00	86
30	0.0002988	80
31	76	74
32	64	68
33	52	62
34	40	57
35	28	51

[a] S = 3.00; a (gas volume) = 2.00.
[b] S = 3.00; a = 10.00.

[44] D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940).

The pressure, P_{CO_2}, of carbon dioxide from the oxidized benzidine is calculated as:

$$P_{CO_2} = p_1 - p_2 - c$$

in which p_1 and p_2 are the manometer readings taken before and after absorption of the carbon dioxide, and c is the value of $p_1 - p_2$ found in the blank analysis.

The sulfate sulfur in the sample is calculated as:

$$\text{mg. S} = P_{CO_2} \times \text{factor}$$

The values of the factor, obtained by calculation and substantiated experimentally, are given in Table XXVI.

B. Determination of Tungsten[45–48]

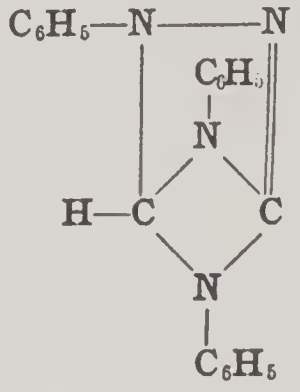
Tungstate ion is quantitatively precipitated by benzidine from acidic solution; the precipitate is probably a mixture of indefinite composition and must be ignited for weighing to tungstic oxide, WO_3. The method affords a separation of tungsten from phosphorus and ferrous iron as well as from arsenic. Precipitation of tungstate in the presence of tartrates is incomplete.

The neutral tungstate solution, containing no more than 300 mg. oxide in 200 ml., is acidified with 1 ml. 1 *N* sulfuric acid and heated to boiling. To the solution is added 30 ml. benzidine hydrochloride reagent, and, when the solution has cooled to room temperature, the precipitate is filtered and washed with a cold solution prepared by diluting 10 ml. of the benzidine hydrochloride reagent to 300 ml. The precipitate is then dried and ignited to tungstic oxide, WO_3, which contains 79.30% tungsten. An alkalimetric method for analyzing the precipitate has been described, but results are not uniformly good.[45]

[45] B. G. Mokeev, *Uchenye Zapiski Kazan. Gosudarst. Univ.*, **90**, 1022 (1930); *Chem. Abstracts*, **26**, 5870 (1932).
[46] G. von Knorre, *Ber.*, **38**, 783 (1905).
[47] J. Lukas and A. Jilek, *Chem. Listy*, **24**, 320 (1930); *Chem. Abstracts*, **24**, 5666 (1930).
[48] H. Wdowiszenski, *Z. anal. Chem.*, **87**, 36 (1931).

II. Nitron

(4,5-Dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole)



Molecular weight: 312.36
Melting point: 189°C.
Solubility: soluble in acetone, benzene, chloroform, ethyl alcohol, ethyl acetate; insoluble in water
Reagent: prepared by dissolving 10 g. nitron in 100 ml. 5% acetic acid, and filtering through a sintered-glass or porcelain filtering crucible; solution should be protected from light

Nitron serves for the precipitation and gravimetric determination of nitrate, perchlorate, perrhenate, and tungstate ions. Numerous other anions, including bromide, chlorate, chromate, iodide, nitrite, and thiocyanate, form insoluble salts with nitron that might interfere, but these may be removed easily by preliminary treatment. Results obtained in the presence of chlorides are generally high, presumably because of coprecipitation.

Nitron nitrate is appreciably soluble in water; 37.1 mg. dissolves per 100 ml. water at 20°C.; at 0° 21.13 mg. per 100 ml. dissolves. If the solution is prepared at a higher temperature and then cooled to 2° or 0°, the saturation concentrations are found to be 53.1 mg. and 33.7 mg., respectively. The solubility is much less in the presence of excess precipitant; if 1 g. nitron is present per 100 ml., the solubility of the nitrate is only 2.0 mg. per 100 ml.[49]

Nitron offers a very convenient method for the gravimetric determination of perrhenate. The precipitate, $C_{20}H_{16}N_4 \cdot HReO_4$ is only slightly soluble in the presence of excess nitron acetate, and is easily dried and weighed.[50] Other rhenium compounds, such as the sulfide,

[49] L. W. Winkler, *Z. angew. Chem.*, **34**, 46 (1921).
[50] W. Geilmann and A. Voigt, *Z. anorg. u. allgem. Chem.*, **193**, 311 (1930).

may be conveniently analyzed by oxidation with hydrogen peroxide to perrhenic acid, followed by precipitation with nitron.[51] Nitron perchlorate, like the nitrate and perrhenate, may be dried and weighed; the tungstate must be ignited to tungstic oxide for final weighing.

A. Determination of Nitrate[49, 52–59]

The neutral solution, containing between 10 and 100 mg. nitrate per 100 ml., and free from interfering anions, is acidified with 1 ml. acetic acid, heated to 60–70°, and treated with 10–15 ml. nitron acetate solution. The solution is cooled in ice water for about 2 hours (or allowed to stand for 24 hours in the dark, at room temperature); the nitron nitrate separates as fine needles. The precipitate is collected on a filtering crucible, utilizing the clear filtrate to transfer the last portions of the solid. The precipitate is washed with about 10 ml. ice water, and is then dried to constant weight at 110°C. The precipitate of $C_{20}H_{16}N_4HNO_3$ contains 16.53% nitrate. Errors are of the order of 0.1 to 0.5%.

Cations are not coprecipitated; neither is an appreciable amount of the reagent.[58] The presence of organic acids—oxalic, lactic, and succinic—is likewise not harmful.[53] Nitrite, if present with nitrate, may be removed by treatment of the sample with hydrazine sulfate; then if (on another sample) the nitrite is oxidized, the total nitrate may be determined; by combining the results of both analyses, the percentages of both nitrate and nitrite may be found.[53] The error in such a method may amount to 0.5% or more.

Methods for the determination of nitrates in meat[60, 61] and in nitrophenols[62] have been reported.

B. Determination of Perrhenate[50, 51]

The neutral solution containing not more than 100 mg. rhenium is adjusted to about 50 ml., and 1 ml. 2 *N* sulfuric acid is added. After

[51] W. Geilmann and F. Weibke, *Z. anorg. u. allgem. Chem.*, **195**, 289 (1931); **199**, 347 (1931).
[52] M. Busch, *Ber.*, **38**, 861 (1905); *Z. anal. Chem.*, **45**, 62 (1906).
[53] H. Franzen and E. Löhmann, *J. prakt. Chem.*, **79**, 330 (1909).
[54] P. Pooth, *Z. anal. Chem.*, **48**, 375 (1909).
[55] W. C. Cope and J. Barab, *J. Am. Chem. Soc.*, **39**, 506 (1917).
[56] W. Mestrezat and M. Delaville, *Bull. soc. chim. biol.*, **8**, 1217 (1926).
[57] J. Grant, *Ind. Chemist*, **8**, 169, 217 (1932).
[58] J. E. Heck, H. Hunt, and M. G. Mellon, *Analyst*, **59**, 18 (1934).
[59] A. Vürtheim, *Rec. trav. chim.*, **46**, 97 (1927).
[60] A. Hes, *Z. anal. Chem.*, **48**, 81 (1909).
[61] C. Paal and A. Ganghofer, *ibid.*, **48**, 545 (1909); *Z. Nahr.-Genussm.*, **19**, 322 (1909).
[62] L. Desvergnes, *Mon. sci.*, **13**, 208 (1923).

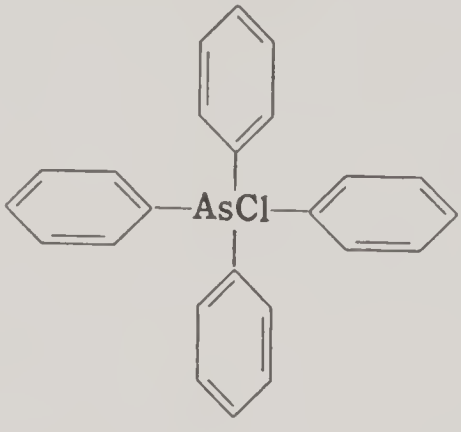
it is heated to about 80°, sufficient 5% nitron acetate solution is added to precipitate the rhenium and leave an excess of 0.3 or 0.4% precipitant. The solution is cooled to room temperature, then kept in ice water for 2 hours, with frequent stirring. The precipitate is collected on a filtering crucible and washed with 10–20 ml. ice-cold nitron acetate solution (0.3%) in 3–5 portions. The precipitate is then washed with two or three 3-ml. portions of a saturated nitron perrhenate solution and dried at 110°C. for 2–3 hours. The precipitate contains 33.06% rhenium, or 44.42% perrhenate ion. Results are generally low by a few tenths of a per cent.

C. Other Determinations

(*1*) Nitron has been used to determine perchlorates in Chile saltpeter, first using De Varda's alloy to reduce the nitrates.[59] (*2*) Alkali tungstates are quantitatively precipitated from weakly acid solution by nitron acetate. Precipitation is made in hot solution; after cooling, the precipitate is filtered, washed with dilute nitron acetate, dried, and ignited to tungstic oxide, WO_3. Rather large errors (0.3% and more) are reported.[63]

III. Tetraphenylarsonium Chloride

$(C_6H_5)_4AsCl$



Molecular weight: 418.8
Solubility: soluble in water
Reagent solution: 0.01 to 0.03 *M* in water

Tetraphenylarsonium chloride forms insoluble salts with a large number of anions, and in many cases the reaction may be made the basis of an analytical method.[64] Among the ions that may be deter-

[63] A. Gutbier and G. L. Weise, *Z. anal. Chem.*, **53**, 426 (1914).
[64] H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186, 269 (1939).

mined are: perchlorate, periodate, permanganate, and perrhenate (and probably others, such as bromide, chromate, fluoride, iodate, iodide, molybdate, thiocyanate, and tungstate, which form insoluble salts with the reagent). The precipitated perrhenate (or other anion) is filtered, washed with water, and dried at 105°C.

The halide complexes of ions such as bismuth, cadmium, gold(III), iron(III), mercury(II), platinum(IV), thallium(III), tin(IV), and zinc also precipitate with the reagent. In general, the chloride complex is most conveniently precipitated. The method requires the use of an excess of standard tetraphenylarsonium chloride in making the precipitation; the excess is determined iodimetrically using the potentiometric end point.

Methods have been developed for the determination of mercury(II) and tin(IV) by precipitaton as $[(C_6H_5)_4As]_2HgCl_4$ and $[(C_6H_5)_4As]_2SnCl_6$, respectively.

Because of the large number of interfering elements, the method is limited to use in cases in which a full knowledge of possible contaminations is available.

A. Determination of Mercury

The solution containing mercury in amounts ranging from 0.5 to 100 mg. is adjusted to 30 ml., and sufficient sodium chloride is added to form a 1.0 to 2.5 *M* solution after the precipitant is added. Standard 0.01 to 0.02 *M* tetraphenylarsonium chloride, in not more than 10-ml. excess, is added with constant stirring. The volume should now be 60 to 120 ml., depending on the amount of mercury present. The precipitate is allowed to stand for 15 to 60 minutes, collected on a Gooch crucible, and washed several times with saturated sodium chloride solution. Filtrate and washings are titrated with standard 0.01 to 0.03 *N* iodine solution (containing 6–8 g. of potassium iodide per liter), using the platinum–calomel electrode system. Near the end point the solution must be saturated with salt before completing the titration. The break in potential at the equivalence point amounts to 25 to 35 mv. per 0.01 ml. 0.02 *N* iodine solution. One ml. 0.010 *M* tetraphenylarsonium chloride is equivalent to 1.0031 mg. mercury. 5- or 10-ml. portions of the tetraphenylarsonium chloride solution are diluted to 100 ml. and titrated in the same manner to prepare the standard solution.

B. Determination of Tin

To the tin solution, as small in volume as possible and containing between 0.8 and 84 mg. tin and none of the previously mentioned interfering ions, is added 2 ml. hydrochloric acid (sp. gr. 1.18) and sufficient sodium chloride (noniodized) to give a 2.5 to 3.0 *M* concentration of sodium chloride in a final volume of 60 ml. A measured excess of standard tetraphenylarsonium chloride solution and enough water to give a volume of 60 ml. are added with constant stirring. If additional reagent is needed to complete the precipitation, no additional salt need be added, but the acid concentration should always be between 0.4 and 1.0 *M*. The concentration of sodium chloride should be 2.5 to 3.0 *M* for quantities of tin up to 30 mg., and may be 1.5 to 2.0 *M* for larger quantities.

When the precipitate has settled completely and has stood for 30 to 60 minutes, it is filtered through a Gooch crucible and washed several times with saturated sodium chloride solution. The combined filtrate and washings are titrated potentiometrically with standard iodine solution (see page 244). One ml. 0.01 *M* tetraphenylarsonium chloride is equivalent to 0.5935 mg. tin.

C. Determination of Cadmium and Zinc

Methods have been described for the determination of these elements by procedures similar to those employed for mercury and tin. For details the original papers should be consulted.

IV. Triphenyltin Chloride

$(C_6H_5)_3SnCl$

Molecular weight: 385.5
Solubility: soluble alcohol; insoluble in water
Reagent solution: 2% in 95% alcohol

Triphenyltin chloride has been proposed as a reagent for the gravimetric determination of fluoride.[65] The reagent precipitates fluoride ion as insoluble triphenyltin fluoride, $(C_6H_5)_3SnF$, which may be filtered easily, dried, and weighed. Since the compound contains a very small amount of fluoride, 5.153%, the method offers advantages for the gravimetric determination of relatively small quantities of fluoride. Furthermore, the method is more rapid than other gravimetric methods for fluoride.

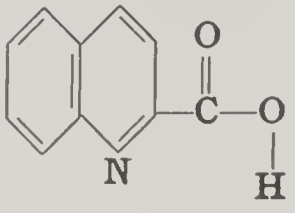
[65] N. Allen and N. H. Furman, *J. Am. Chem. Soc.*, **54**, 4625 (1932).

Among the disadvantages in the use of the reagent is the fact that, because the precipitate is fairly soluble, it must be washed with a solution saturated with triphenyltin fluoride. The method is most satisfactory with 40 mg. or less of fluoride; the smallest amount determinable is about 0.05 mg. At this lower concentration the errors are of the order of 15%, but are much less with larger quantities. The errors tend to be positive, primarily because the reagent is insoluble in water and tends to coprecipitate; foreign electrolytes tend to promote this.

The solution to be analyzed should contain no more than 40 mg. fluoride, and should have a *p*H between 7 and 9. To the solution is added 95% alcohol so that it will comprise 60 to 70% of the final volume. The solution is heated to boiling and treated with a boiling solution made up of twice the required amount of triphenyltin chloride solution and an equal volume of alcohol. The precipitant is run slowly into the hot fluoride solution, with vigorous stirring, and the mixture is again heated to boiling. The solution is allowed to cool, with stirring, and then allowed to stand overnight. When the quantity of precipitate is small, the solution should be cooled in an ice bath for 1 hour prior to filtration. The precipitate is collected on a sintered-glass or porous porcelain filtering crucible, washed with 95% alcohol saturated with triphenyltin fluoride, about 50 ml. being used. The precipitate is dried for 30 minutes at 110°C., cooled, and weighed as $(C_6H_5)_3SnF$, which contains 5.153% fluorine. The precipitate is not hygroscopic.

CHAPTER XVI

Quinaldic Acid



Molecular weight, 173.2
Melting point: 155–157°C.
Solubility: soluble in water, alcohol, ether
Reagent solution: as desired, 1–3% solution of the acid or its sodium salt in water; stable over period of several weeks when stored in amber bottles

Quinaldic acid has been used for the determination of cadmium, copper, and zinc, either separately or in the presence of certain other ions; also, for the colorimetric determination of ferrous iron and, to a limited extent, for the gravimetric determination of uranium. The functional group contained in the reagent and the type of complex that is formed have been discussed earlier (Chap. I). Among the ions which combine with quinaldic acid to form insoluble salts are: cadmium, cobalt, copper, iron(II, III), lead, mercury(I, II), molybdate, nickel, palladium(II), platinum(II), silver, tungstate, and zinc. Basic salts of aluminum and chromium are formed with quinaldic acid.

The formation of the insoluble quinaldates (with the probable exception of aluminum, chromium, molybdate, and tungstate complexes whose compositions are uncertain) is conditioned by the *p*H, as described in Chapter III. Thus, separations may be made through control of the *p*H. Copper quinaldate, one of the least soluble salts, may be precipitated from relatively acidic solutions, while under the same conditions the more soluble zinc and cadmium quinaldates do not precipitate. In Table XXVII are given some *p*H values for incipient and complete precipitation of various amounts of zinc, copper, and cadmium ions with various quantities of quinaldic acid. These values have been calculated by the methods outlined on page 59. The solubility

products from which the calculations are made are contained in Table XXVIII.

TABLE XXVII

*p*H for Precipitation of Ions with 50% Mole Excess Quinaldic Acid

Ion	Concentration, moles per liter				
	0.001	0.003	0.005	0.008	0.01
Cadmium					
Incipient	2.79	2.07	1.74	1.44	1.29
Complete	4.75	4.03	3.70	3.40	3.25
Copper					
Incipient	0.54	*ca.* 0	<0	<0	<0
Complete	2.50	1.78	1.45	1.15	1.00
Zinc					
Incipient	2.04	1.32	0.99	0.69	0.54
Complete	4.00	3.28	2.95	2.65	2.50

Cadmium, cobalt, copper, nickel, silver, and zinc quinaldates are soluble in excess ammonia. A large excess of sodium or potassium hydroxide will likewise decompose the complexes, yielding sodium quinaldate and the metallic hydroxide.

TABLE XXVIII

Solubility Products of Quinaldates[a]

Element	*p*S[b]
Cadmium	12.3
Cobalt	10.8
Copper	16.8
Iron(III)	16.9
Lead	10.6
Mercury(I)	17.9
Mercury(II)	16.8
Nickel	10.1
Palladium	12.9
Silver	17.9
Zinc	13.8

[a] J. F. Flagg and F. T. McClure, *J. Am. Chem. Soc.*, **65**, 2346 (1943).
[b] *p*S = −log solubility product.

Use of the molybdate and tungstate complexes in analytical work has not been reported, although the tungstate complex is precipitated

quantitatively between *p*H 0 and *p*H 1.[1] Neither of these ions forms precipitates with quinaldic acid above *p*H 4.

By the use of complexing agents, zinc may be determined in the presence of copper, silver, and mercury,[2] and copper may be determined in steels.[3, 4] In the first case, copper is reduced to the cuprous state with sulfurous acid. Thiourea is then added, forming complexes with the cuprous, silver, and mercuric ions from which the corresponding metals cannot be precipitated by quinaldic acid. Zinc, however, is precipitated by the reagent, and thus a separation is effected. In the second case, interference of iron with the precipitation of copper is minimized through the use of tartaric acid to keep the iron in solution as a soluble complex.

The quinaldates of cadmium, copper, and zinc are well-defined crystalline salts, easily filtered, washed, and dried. The copper salt is pale blue; the other two salts are white. They are dissolved by chloroform, and decomposed by strong acids. This latter reaction may be used for the recovery of quinaldic acid from quinaldate precipitates. The precipitates are dissolved in acid; the metal is precipitated at the proper *p*H with hydrogen sulfide; and the quinaldic acid is recovered from the solution by filtration and evaporation. All quinaldic acid determinations are concluded gravimetrically, since there is no satisfactory method at present for analyzing the precipitates volumetrically.

One method that has been tried* with limited success involves oxidation of the precipitates with alkaline permanganate. Using Stamm's procedure,[5] the quinaldic acid portion of the complex can be oxidized quantitatively to quinolinetricarboxylic acid(2,5,6). The procedure is slow and troublesome, and offers no advantage over the gravimetric method. Oxidation with nitrato cerate (see page 89) might be more convenient, but does not appear to have been tried. Polarographic techniques (see page 256) may also hold promise.

The uranium complex must be ignited to U_3O_8 for final weighing:

* Unpublished work by Lloyd Mitchell.

[1] J. F. Flagg and F. T. McClure, *J. Am. Chem. Soc.*, **65**, 2346 (1943).

[2] P. R. Ray and N. K. Dutt, *Z. anal. Chem.*, **115**, 265 (1939).

[3] A. M. Zanko and G. A. Butenko, *Zavodskaya Lab.*, **6**, 545 (1937); *Ber. Inst. physik. Chem. Akad. Wiss. Ukr. S.S.R.*, **9**, 99 (1938); *Chem. Abstracts*, **34**, 687 (1940).

[4] J. F. Flagg and D. W. Vanas, *Ind. Eng. Chem., Anal. Ed.*, **18**, 436 (1946).

[5] Quoted in R. Oesper. *Newer Methods of Volumetric Chemical Analysis.* Van Nostrand, New York, 1938, p. 55 ff.

consequently, quinaldic acid is less desirable for the determination of this element than other precipitants, *e.g.*, 8-hydroxyquinoline, whose uranium complex may be weighed directly.

I. Determination of Copper[6]

The solution to be analyzed should contain no more than 100 mg. copper in 150 ml. and should be free from elements other than the alkali metals or alkaline earths. The *p*H is adjusted as required (depending on the copper content and the amount of precipitant to be used), using a universal indicator paper or glass-electrode *p*H meter. For solutions containing only copper, careful *p*H adjustment is not required, and any value from *p*H 2 to 5 will serve. The solution may contain nitric, hydrochloric, or sulfuric acids; acetates are permissible only in limited amounts.* The solution is heated to boiling, and quinaldic acid (sodium salt or free acid) solution is added in 25–50% excess above that required to precipitate the copper. The precipitate is stirred vigorously and, after it has stood for 5–10 minutes, it is washed with 50–100 ml. hot water decanted through a filtering crucible of fine porosity. Finally, the precipitate is transferred to the crucible, washed with 100–200 ml. hot water, and dried to constant weight at 110–115°C. The precipitate of $(C_{10}H_6NO_2)_2Cu \cdot H_2O$ contains 14.94% copper.

A. Determination of Copper[6] in the Presence of Lead, Phosphoric Acid, Arsenious and Arsenic Acids

To the solution containing 0.1 g. copper (or less) in about 200 ml. is added 10 ml. glacial acetic acid. The *p*H should be about 2 to 2.5. The solution is heated to boiling and sodium quinaldate is added dropwise with stirring until precipitation is complete; then 1–2 ml. in excess is added. After it has been standing for 10–15 minutes, the solution is decanted through a filtering crucible of fine porosity, and the precipitate is washed several times with small portions of a solution containing 2 ml. glacial acetic acid and 5 drops sodium quinaldate solution per 100 ml. water. The precipitate is transferred to the crucible, washed with 100 ml. hot water, and dried to constant weight at 115°C. The precipitate of $Cu(C_{10}H_6NO_2)_2 \cdot H_2O$ contains 14.94% copper.

* Sodium acetate is reported to have a specific solvent effect on copper quinaldate (R. J. Shennan, *Analyst*, **64**, 14 (1939). Acetic acid has a similar effect [A. K. Majumdar, *Analyst*, **68**, 242 (1943)], dissolving ten times as much copper quinaldate as a sulfuric acid solution of the same *p*H (2.05).

[6] P. R. Ray and M. K. Bose, *Z. anal. Chem.*, **95**, 400 (1933).

B. Determination of Copper[6] in the Presence of Manganese, Nickel, and Cobalt

The solution, containing no more than 0.1 g. copper, is acidified with 5–8 ml. 2 *N* sulfuric acid and made up to 200 ml. The solution is heated to boiling and the copper quinaldate precipitated in the manner described previously. The precipitate is washed with a hot solution containing 2.5 ml. 2*N* sulfuric acid and 1 ml. sodium quinaldate reagent per 100 ml., then with hot water. It is dried at 115°C. and weighed as $Cu(C_{10}H_6NO_2)_2 \cdot H_2O$ containing 14.94% copper.

C. Determination of Copper in the Presence of Cadmium

Satisfactory results in the separation of 26–53 mg. copper from 31–92 mg. cadmium, using the procedure of Ray and Bose,[6] have been claimed.[7] The precipitation of copper is made in sulfuric acid solution at a *p*H of 2 or slightly higher. Spectrochemical[8] and x-ray[9] examination of the copper quinaldate precipitates revealed that negligible quantities of cadmium quinaldate were present.

Nevertheless, this method should be employed cautiously, particularly when the approximate quantities of cadmium and copper are unknown. Potential sources of error are to be found in the incomplete precipitation of copper if the *p*H for precipitation is too low, or in the coprecipitation of cadmium if the *p*H is too high. For the separation of cadmium and copper a reagent whose cadmium salt is very soluble in acid solution is to be preferred. Salicylaldoxime (page 259) meets this requirement, and is preferable to quinaldic acid for making this separation.

D. Microdetermination of Copper and Separation of Copper from Phosphoric, Arsenious, and Arsenic Acids[10, 11]

The method follows, in a general way, the one given for the macrogravimetric determination of copper. The precipitate of copper quinaldate is formed from a weakly acid solution, dried at 125°C., and weighed as the monohydrate $Cu(C_{10}H_6NO_2)_2 \cdot H_2O$. The determination requires the use of a microbeaker and filter stick.

The neutral solution containing from 0.1 to 1 mg. copper in a vol-

[7] A. K. Majumdar, *Analyst*, **68**, 242 (1943).
[8] A. K. Majumdar, *J. Indian Chem. Soc.*, **21**, 24 (1944).
[9] C. E. Pritchard and R. C. Chirnside, *Analyst*, **68**, 244 (1943).
[10] P. R. Ray and M. K. Bose, *Mikrochemie*, **17**, 11 (1935).
[11] P. R. Ray and R. Gupta, *ibid.*, **17**, 14 (1935).

ume of 1 to 2 ml. is acidified with 1 drop 0.7 *N* sulfuric acid. The beaker is placed on a water bath and, when hot (75–85°), treated with the quinaldic acid reagent. The reagent is added dropwise, swirling the beaker gently between drops and waiting for the precipitate to settle before adding more. When precipitation is thought to be complete, an additional 0.1 ml. of the reagent is added and the mixture is kept on the water bath for 10 minutes longer. The supernatant liquid is drawn off through the filter stick and the precipitate is washed by decantation with six 1-ml. portions of hot water, keeping the beaker on the water bath or on an aluminum heating block. Care should be exercised to prevent, as far as possible, any precipitate from collecting on the filter, since this retards the rate of filtration. Finally, the liquid is removed completely and the beaker and filter stick are dried at 125° in an apparatus designed especially for the purpose.[12] The precipitate contains 14.94% copper.

E. Determination of Copper in Cast Iron and Steel[4]

A factor weight sample of the material (1.494 g.) is dissolved in 15–20 ml. aqua regia. When reaction is complete, 10 ml. sulfuric acid (1:1) is added and the solution is evaporated to fumes of sulfur trioxide. The residue is taken up in 50 ml. water containing a little sulfuric acid (1:4) to dissolve salts. The solution is filtered on Whatman No. 40 paper, and the residue is washed once with water, then with 25 ml. of a neutral or weakly alkaline solution containing 10 g. tartaric acid, and finally with water. Concentrated ammonium hydroxide is added to filtrate and washings until they turn a deep cherry-red color. Upon cooling, the *p*H is adjusted to about 3 by the addition of diluted ammonia (1:3) or diluted sulfuric acid (1:4). The solution is heated to about 75°, and 5 ml. sodium quinaldate solution (1%) is added for each mg. copper present. After being digested on the steam bath for 30 minutes, the solution is allowed to cool and the copper quinaldate is collected on a filtering crucible and washed with cold water. The filtering crucible is then placed in an apparatus designed for the quantitative recovery of the filtrate (Fisher Filtrator), and the precipitate is dissolved in a few milliliters of hot (1:1) hydrochloric acid. The crucible is rinsed with several small portions of hot acid and finally with hot water. To the filtrate 2 g. tartaric acid and 2 ml. sodium quinaldate reagent are added, and the *p*H is adjusted to about 3 with ammonium hydroxide (1:4). The precipitate is digested, cooled, fil-

[12] A. Benedetti-Pichler, *Mikrochemie*, Pregl-Festschrift, 6 (1929).

tered as before, and washed with cold water. The precipitate is dried to constant weight at 115–120°C.

*Preliminary Separation by Internal Electrolysis.** A one to two gram sample of the material is dissolved in 15–20 ml. aqua regia; 3 ml. concentrated sulfuric acid is added, and the solution is evaporated to fumes. The residue is taken up with about 10 ml. water; the solution is heated to boiling, and 1.2 g. hydroxylamine hydrochloride in 10 ml. water is added. Two milliliters hydrochloric acid (1:1) and 2 ml. nitric acid (1:3) are added; the bound electrodes are inserted, and the electrolysis is continued for 30–45 minutes at 70°. The electrodes consist of a platinum gauze cathode and a 23-cm. length of aluminum wire bent into a spiral or simple loop as the anode; these are connected at the top by means of a conducting clip which holds the anode rigidly inside the cathode. The electrodes are then removed (with washing) and the deposit is dissolved in the minimum quantity of concentrated nitric acid (not exceeding a few ml.).

The solution is transferred to a 150-ml. beaker; 2 g. ammonium acetate is added, and the *p*H is adjusted to 3 to 3.5 with ammonia. After being diluted to about 100 ml., the solution is analyzed for copper by precipitation with quinaldic acid as described on page 250.

II. Determination of Cadmium[5]

The solution to be analyzed should contain no more than 0.1 g. cadmium in 150–200 ml., and should be slightly acidic. Elements other than the alkali metals or alkaline earths should be absent. The calculated amount of sodium quinaldate reagent is added with stirring, followed by 25% excess. Dilute (2–3 *N*) sodium hydroxide is then added until a dense, white, granular precipitate forms. The *p*H should be 4–5, since, at a higher *p*H, basic salts may form. The precipitate is stirred well and allowed to settle, and the solution is decanted through a filtering crucible of fine porosity. The precipitate is washed with several 50 to 100-ml. portions of cold water, transferred, and dried to constant weight at 125°C. The precipitate of $Cd(C_{10}H_6NO_2)_2$ contains 24.62% cadmium.

III. Determination of Zinc[6]

The solution to be analyzed should be free from elements other than alkali metals or alkaline earths, and should contain no more than 0.1 g. zinc in a total volume of 150 ml.; it is acidified with 2–5 ml. dilute

* For a general discussion of internal electrolysis, see H. H. Willard and H. Diehl, *Advanced Quantitative Analysis*. Van Nostrand, New York, 1943, pp. 60–63.

acetic acid (to *p*H 3–4) and heated to boiling. Sodium quinaldate solution is then added until precipitation is complete; an excess of 25% should be used. The precipitate is washed by decantation, collected on a filtering crucible of fine porosity, washed, and dried at 125°C. to constant weight. The precipitate of $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$ contains 15.29% zinc.

A. Determination of Zinc[13] in the Presence of Phosphoric Acid

The solution, containing no more than 0.1 g. zinc and phosphoric acid in 150–200 ml., is treated with sodium carbonate until a turbidity appears. Enough glacial acetic acid is added to clear the turbidity and, to provide several milliliters in excess; the *p*H should be 3–4. The solution is heated to boiling (during which time the solution must remain clear) and the zinc is precipitated in the usual way.

B. Determination of Zinc[13] in the Presence of Iron, Aluminum, Uranium, Beryllium, and Titanium

The solution, containing no more than 0.1 g. zinc in 100 ml., is treated with a few milliliters of bromine water and is boiled. Upon cooling, 5 g. sodium tartrate is added and the solution is neutralized with ammonia to *p*H 5. The solution is diluted to 150–175 ml., heated to 50°C., and the zinc is precipitated by dropwise addition of sodium (or ammonium) quinaldate solution, using a slight excess. After it has settled, the precipitate is filtered, washed with hot water, and dried to constant weight at 125°C. Errors in this separation may arise from the use of too much ammonia which tends to dissolve the zinc quinaldate, or from coprecipitated impurities in the zinc quinaldate. The method should afford a useful separation, but conditions might well warrant a more thorough investigation.

C. Determination of Zinc in the Presence of Copper, Mercury, and Silver

To the solution containing not more than 0.1 g. zinc in addition to the other elements, are added 8 g. potassium iodide, 5 ml. 6 *N* acetic acid, a freshly prepared solution containing 4–8 g. sodium bisulfite, and a solution containing 6 g. thiourea. The mixture is heated to boiling and the zinc is precipitated as described previously.

[13] P. R. Ray and A. K. Majundar, *Z. anal. Chem.*, **100**, 324 (1935).

D. Microdetermination of Zinc[10]

1. Alone, or in the Presence of the Alkali Metals

The conditions required for the microgravimetric method are similar to those for the macrogravimetric method. A filter stick and microbeaker are used for carrying out the determination. The solution, containing from 0.09 to 1 mg. zinc in a volume of 1 to 1.5 ml., is acidified with 0.02 to 0.04 ml. glacial acetic acid and heated to about 60°C. on a water bath. Then, while the beaker is swirled, the zinc is precipitated by the dropwise addition of the quinaldic acid reagent, using an excess of 0.2 to 0.25 ml. above the theoretical amount. Heating is continued for about 5 minutes, after which the precipitate is allowed to stand for 10–15 minutes. The supernatant liquid is carefully drawn off, and the precipitate is washed by decantation with five or six 1-ml. portions of hot water. Beaker and filter stick are dried at 125°; the precipitate of zinc quinaldate, $(C_{10}H_6NO_2)_2Zn \cdot H_2O$ contains 15.29% zinc.

2. In the Presence of Copper, Silver, and Mercury

For the determination of zinc in the presence of copper, silver, or mercury, a procedure similar to that used in the macromethod is followed.[14]

The solution, containing zinc as the sulfate and not exceeding 1 ml. in volume, is treated in a microbeaker with 0.3 to 0.5 ml. freshly prepared 20% sodium bisulfite solution. Then 0.05 ml. glacial acetic acid is added, followed by 1 to 1.5 ml. 10% thiourea solution. A white precipitate is formed which dissolves slowly in the cold, and more rapidly upon heating. Zinc is then precipitated with quinaldic acid as in the method given previously, and the determination is concluded in the same manner. When no copper is present, the treatment with bisulfite may be omitted.

3. In the Presence of the Alkaline Earth Metals, Magnesium, Manganese, and Phosphoric Acid

Zinc may be separated from the alkaline earth metals, magnesium, manganese, and phosphoric acid by a method resembling that used in determining zinc in relatively pure solutions.[10, 11] In this case more acetic acid should be used than is used in the simple zinc determina-

[14] P. R. Ray and T. C. Sarkar, *Mikrochemie*, **27**, 64 (1939).

tion; 0.05 to 0.1 ml. is required, particularly if manganese is present. The precipitate of zinc quinaldate is washed 3 times with a wash solution containing 2.5 ml. glacial acetic acid and 5 ml. 1% sodium quinaldate per 100 ml., using portions of from 0.5 to 1 ml. Finally, the precipitate is washed with 3 similar portions of hot water, and dried as usual. The method has been shown to yield satisfactory results with 0.2 to 0.75 mg. zinc in the presence of 0.75 to 2.5 mg. manganese.

4. In the Presence of Aluminum and Iron[15]

The neutral solution, containing 0.15 to 1 mg. zinc in a total volume of 2 to 2.5 ml. and up to several milligrams of iron and(or) aluminum, is treated with 0.4 to 1 ml. (depending on the amounts of foreign elements present) 5% sodium tartrate solution. An air stream containing ammonia is blown on the surface of the solution until the odor of ammonia persists. (The stream of air with ammonia is obtained by passing air through a 10% ammonia solution. The stream of air is directed upon the surface of the solution by means of a capillary, held about 1.5 cm. above the surface of the liquid.) The solution in the beaker is swirled, and the zinc is precipitated by dropwise addition of sodium quinaldate reagent of a strength corresponding to 1 g. quinaldic acid per 100 ml. An excess of about 0.25 ml. is used. Since zinc quinaldate is soluble in ammoniacal solutions, the excess ammonia must be removed by heating the solution to about 60°C. and passing an air stream from a capillary over the surface of the solution. Heating should not be prolonged unnecessarily. When ammonia has been removed, the solution is cooled quickly; the precipitate is filtered and washed as before, and the determination is concluded in the usual manner.

IV. Polarography of Quinaldic Acid

The behavior of quinaldic acid at the dropping mercury electrode has been studied carefully,[16] and the information available should prove of value in the direct determination of quinaldic acid, in amperometric titrations of metallic ions with the reagent, in measurements of solubility of quinaldates, or in all of these.

Reduction of quinaldic acid occurs at the dropping mercury electrode in well-buffered solutions over the entire *p*H range of from 1.5

[15] P. R. Ray and M. K. Bose, *Mikrochemie*, **18**, 89 (1935).
[16] J. T. Stock, *J. Chem. Soc.*, **1944**, 427.

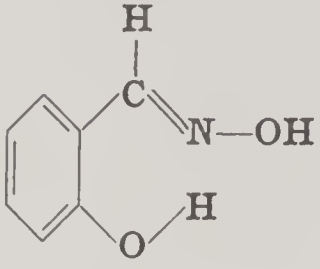
to 12. At *p*H 1.5, two reduction waves are seen at applied potentials of approximately 0.6 and 0.9 v. The second wave vanishes at *p*H 4 but as the neutral point is approached the polarographic spectrum becomes much more complicated, with a total of four waves appearing. The potential of the first (and analytically important) wave shifts to more negative values as the *p*H increases; up to *p*H 6 the half-wave potential is given by:

$$E_{1/2} = -(0.52 + 0.06\ p\mathrm{H})\ \text{v., } vs.\ \text{S.C.E.}$$

The height of the first wave also varies with the *p*H, but is directly proportional (at constant *p*H) to the concentration of quinaldic acid, at least with concentrations up to 2×10^{-3} *M*. In alkaline solutions the concentration of quinaldic acid is proportional to the sum of the first and last waves. The first reduction wave corresponds to a 2-electron process, and the reduction product is presumably dihydroquinaldic acid.

CHAPTER XVII

Salicylaldoxime



Molecular weight: 137.1
Melting point: 55–57°C.
Solubility: soluble in alcohol, acetone, ether; slightly soluble in petroleum ether, water
Reagent solution: prepared by either of 2 methods: (*a*) dissolve 1 g. salicylaldoxime in 5 ml. alcohol, pour slowly with stirring into 95 ml. water at 86°C. (*b*) Add 2.22 g. salicylaldehyde in 8 ml. alcohol to 1.27 g. hydroxylamine hydrochloride in 2 ml. water; dilute with 15 ml. alcohol, pour slowly with stirring into 225 ml. water at 80°C.[1]; the solution should be filtered if not clear after several hours; salicylaldoxime solutions should be kept in amber bottles

Ephraim[2] was the first to note that the oxime of salicylaldehyde had potentialities as an inorganic analytical reagent; he described many of its reactions with inorganic ions. The principal use of salicylaldoxime has been in the determination of copper although, as Table XXIX shows, it combines with numerous other ions, under diverse conditions of acidity.

In addition to the elements listed above with which salicylaldoxime forms precipitates, the reagent also forms soluble colored compounds with iron(III), uranyl ions, and with osmic acid.

The salicylaldoxime complexes form readily and possess desirable analytical properties; they are easily filtered, washed, and dried, and are stable and of definite composition. The precipitates may be analyzed volumetrically, either by means of permanganate, or bromate–bromide reagent. In the first method[3, 4] the organometallic compound,

[1] S. Astin and H. L. Riley, *J. Chem. Soc.*, **1933**, 314.
[2] F. Ephraim, *Ber.*, **63**, 1928 (1930); **B64**, 1210, 1215, 2819 (1931).
[3] B. Tougarinoff, *Ann. soc. sci. Bruxelles*, **54B**, 314 (1934).
[4] M. Gahide, *Bull. soc. chim. Belg.*, **45**, 9 (1936).

TABLE XXIX

Ions Which Yield Precipitates with Salicylaldoxime[a]

Ion	Color of precipitate	Approximate *p*H for incipient precipitation, 0.001 *M* solution
Silver	Light yellow	6.3
Lead	Yellow	5
Mercury(II)	Light yellow	5.3
Copper	Greenish yellow	<0
Cadmium	Light yellow	7
Bismuth	Bright yellow	7
Manganese(II)	Brown	8.9
Iron(II)	Brown	7
Cobalt	Brown	5.5
Nickel	Green	3.3
Zinc	Light yellow	6.5
Palladium(II)	Yellow	"Acid"
Magnesium	Light yellow	10 or more
Vanadate	Black	<0

[a] J. F. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 520 (1940).

after being filtered and washed, is decomposed with sulfuric acid and excess ferric sulfate solution is added to it. The ferrous ion produced by the reducing action of hydroxylamine is then determined with permanganate. This method, although slow, gives satisfactory results on the semimicro scale. The bromate method[5] depends on simultaneous bromination of the salicylaldehyde molecule and oxidation of the hydroxylamine by an excess of standard bromate–bromide solution. The excess bromate may be determined by titration with arsenite.

The copper salt of salicylaldoxime is soluble in 0.01 *N* hydrochloric acid to the extent of about 2.2×10^{-4} mole per liter, a value comparable with the solubility of copper hydroxyquinolate and anthranilate.[6] The solubilities of other complexes have not been reported, but, again, a rather low order of solubility might be expected.

I. Determination of Copper

According to careful studies of Biefeld and Howe,[7] the copper complex is precipitated quantitatively at *p*H 2.6 and higher from solutions containing 25 mg. copper per 100 ml. and a 50% excess of reagent. At this *p*H relatively little interference from other ions is encountered

[5] N. H. Furman and J. F. Flagg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 738 (1940).
[6] W. D. Treadwell and A. Ammann, *Helv. Chim. Acta*, **21**, 1249 (1938).
[7] L. P. Biefeld and D. E. Howe, *Ind. Eng. Chem., Anal. Ed.*, **11**, 251 (1939).

(Table XXIX). If nickel is present in a comparable amount, the *p*H must be kept below 3.1—the point of incipient precipitation of the nickel complex.

To the solution containing not more than 100 mg. copper in 150–200 ml. is added sodium hydroxide to produce a precipitate. Acetic acid is added to bring the *p*H to 3 or slightly less, and salicylaldoxime reagent is added slowly with stirring to the cold solution. A few milliliters excess should be added. When the precipitate has coagulated it is collected on a filtering crucible of fine porosity and washed with cold water until the washings no longer give a purple color when tested with ferric chloride solution. The precipitate of $Cu(C_7H_6O_2N)_2$ is dried at 100–105°C. and weighed as such. It contains 18.94% copper.

The precipitate may be analyzed volumetrically by the method used for copper α-benzoin oxime precipitates (page 123). In this instance a definite number of equivalents is consumed per gram-atom of copper, but no simple equation can be written for the process, which must be regarded as an empirical one. It is recommended that the method not be used in determining more than 15–18 mg. copper; amounts down to 1 mg. may be determined very easily, and generally with an accuracy of 1% or less. Under the conditions specified, 14 equivalents of oxidant are used per mole copper salicylaldoxime. The milliequivalent weight of copper is 0.004541 g.; hence, 1 ml. 0.1 *N* bromate equals 0.4541 mg. copper.

Iron(III) is entrained by the copper complex,[7] so that if the amount of iron in solution with the copper exceeds a few milligrams, results will be high. Use of hydrochloric acid rather than acetic acid is said to minimize this error, as will precipitation from a tartrate solution.[8]

A. Microdetermination of Copper

The microgravimetric method follows the general method outlined above.[9, 10] The solution should be freed from large amounts of acid, by evaporation if necessary. The residue is taken up in a few drops of diluted nitric acid (1:20), and the solution is transferred to a filter beaker. The total volume, including washings, may be 2 to 3 ml. at this point. The acid solution is neutralized to a permanent turbidity with 1% sodium hydroxide solution, followed by diluted acetic acid

[8] W. Reif, *Z. anal. Chem.*, **88**, 38 (1932).
[9] F. Hecht and R. Reissner, *Mikrochemie*, **17**, 130 (1935).
[10] W. Reif, *ibid.*, **9**, 424 (1931).

(1:4) to just clear the solution. Salicylaldoxime is added and the mixture is shaken to coagulate the precipitate. After standing for 5–10 minutes the solution is drawn off; the precipitate is washed with cold water until free from excess salicylaldoxime, and dried at 100–105°C. to constant weight.

B. Determination of Copper in Alloys

The reagent may be used to advantage for determining copper in certain nonferrous and ferrous alloys.

1. Nonferrous alloys[7, 11]

Brass and bronze, as well as zinc, magnesium, and aluminum alloys, may be analyzed for copper with salicylaldoxime. The sample weighed out to contain no more than 100 mg. copper, is dissolved in the minimum quantity of nitric acid. Tin, if present, must be removed by the conventional procedures. Copper is determined in the tin-free filtrate as described above. Triplicate analyses should require about 2 hours, if removal of tin is not necessary.

2. Steel[12, 13]

Methods have been reported for the direct determination of copper in steel, using tartaric acid to prevent contamination of the copper precipitate with iron. Details on the reliability of these methods are lacking; it is expected that difficulties similar to those encountered in using quinaldic acid might be found (see page 252).

C. Miscellaneous Determinations

The separation of copper and nickel has been studied[7, 14]; also, the separation of copper and cadmium, and copper and lead.[15] A method for the determination of copper in pyrites has been given.[16] The amperometric titration of salicylaldoxime with copper, and its use in the determination of copper, has been described by Neuberger.[17]

[11] M. Chambers, *Chemist-Analyst*, **26**, 52 (1932).
[12] E. Stengel, *Tech. Mitt. Krupp Forsch. Ber.*, **2**, 87 (1939); *Chem. Abstracts*, **33**, 8521 (1939).
[13] M. Jean, *Bull. soc. chim.*, **10**, 201 (1943); *Chem. Abstracts*, **38**, 6230 (1944).
[14] H. L. Riley, *J. Chem. Soc.*, **1933**, 895.
[15] M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan*, **55**, 1060 (1934).
[16] I. Ubaldini, *Chimica e industria*, **19**, 65 (1937).
[17] A. Neuberger, *Arch. Eisenhüttenw.*, **13**, 171 (1939); *Chem. Abstracts*, **34**, 343 (1940).

II. Other Applications of Salicylaldoxime

Bismuth. Salicylaldoxime forms an insoluble basic salt of unknown composition with bismuth ions in almost neutral solution. The precipitate must be ignited to Bi_2O_3 for weighing.[18]

Lead. At *p*H 8.9 or higher, lead is quantitatively precipitated as $PbC_7H_5O_2N$. The precipitate is dried at 105°C. Use of a strongly ammoniacal solution permits the separation of lead from silver, zinc, and cadmium.[19, 20]

Palladium. Divalent palladium ions are precipitated quantitatively from acid solution as $Pd(C_7H_6O_2N)_2$. The precipitate can be weighed after drying at 110°C.; it contains 28.17% palladium. Palladium is separated from platinum by this method.[21] A volumetric method has also been described.[4]

Zinc. Salicylaldoxime precipitates zinc as either $Zn(C_7H_6O_2N)_2$ or $ZnC_7H_5O_2N$. Rigidly prescribed conditions must be followed for quantitative results,[18, 22, 23] and the use of anthranilic acid, 8-hydroxyquinoline, or quinaldic acid seems better suited for the determination of this element.

[18] J. F. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 663 (1940).
[19] M. Ishibashi and H. Kishi, *Bull. Chem. Soc. Japan*, **10**, 362 (1935).
[20] W. B. Ligett and L. P. Biefeld, *Ind. Eng. Chem., Anal. Ed.*, **13**, 813 (1941).
[21] H. Holzer, *Z. anal. Chem.*, **95**, 392 (1933).
[22] T. G. Pearson, *ibid.*, **112**, 179 (1938).
[23] L. P. Biefeld and W. B. Ligett, *Ind. Eng. Chem., Anal. Ed.*, **14**, 359 (1942).

CHAPTER XVIII

Tannin

(Digallic Acid, $C_{14}H_{10}O_9$)

Molecular weight: 322. 2
Melting point: 268–270°C. (dec.)
Solubility: soluble in alcohol, water; insoluble in chloroform, ether
Reagent solution: 2% aqueous solution freshly prepared

The usefulness of tannin in making certain difficult separations justifies its inclusion in this book, although it cannot be thought of as an "organic reagent" in the sense of most of the other reagents that have been discussed. The precipitates formed by tannin and inorganic ions lack many of the very properties, such as stability, definite composition, and well-defined crystalline form, which distinguish most organometallic precipitates. The great value of tannin lies in its ability to precipitate quantitatively, alone or in conjunction with another reagent, with a minimum of interference, elements which are notably difficult to determine: columbium, tantalum, and tungsten. The precipitation reactions are not confined to these elements alone, however. Although a somewhat selective action is obtained when a mineral acid solution is employed, this action is lost at higher *p*H values, as in an acetate buffer; aluminum, beryllium, chromium(III), copper, gallium, iron(III), manganese(II), thorium, tin(IV), titanium, uranium(VI), vanadium, and zirconium are precipitated. Cobalt, cadmium, nickel, and zinc are ordinarily not precipitated by tannin.

The exact nature of the reaction between tannin and the inorganic ions remains obscure, although, in view of the large number of elements precipitated under conditions that favor the formation of hydrous oxides, the possibility of "adsorption" or an equivalent process cannot be disregarded as an important factor in the precipitation. Tannin is a negative colloid, capable of flocculating positive colloids, such as the metal sols. On this basis, the precipitation would be the result of neutralization of charges on oppositely charged colloids, with resultant flocculation. Comparatively little information is available

on this subject; however, it is known that in somewhat similar cases of dye adsorption, a definitely nonstoichiometric combination occurs.[1]

The tannin precipitates are characterized by being flocculent, although when filtered under gentle suction the bulk is greatly reduced. For washing the precipitates a solution containing a volatile electrolyte and a little tannin is used. The precipitates are always ignited to the corresponding oxides for final weighing. In the following sections, some of the more common uses of tannin will be described.

I. Separation and Determination of Columbium and Tantalum[2–6]

The separation of columbium and tantalum from elements with which they are often associated—iron, the rare earths, silicon, thorium, tin, titanium, tungsten, vanadium, and zirconium—is necessarily complicated, and, for a complete discussion of the chemistry involved, reference should be made to the original sources, or to summaries such as that given by Schoeller.[7] At this point, interest centers on the separation of columbium and tantalum in a mixture of their oxides, free from other elements. The method depends on the fact that tannin will precipitate tantalum more easily than columbium from a solution of the oxalate complexes of those elements. The solution must be slightly acidic to precipitate the yellow tantalum compound. From a neutral solution, and with excess tannin present, an orange columbium compound precipitates. Since the tantalum precipitate is rarely free from columbium, reprecipitations are required. The color of the tantalum precipitate serves to indicate the extent of contamination by columbium; a pure yellow precipitate is generally columbium-free, while one tinted with orange is not. Unless the tantalum is present in large excess, a number of reprecipitations may be required to free the tantalum of columbium.

A sample of the mixed oxides, weighing not more than 500 mg. and containing no more than 250 mg. tantalic oxide, Ta_2O_5, is fused with 3 to 6 g. dehydrated potassium pyrosulfate in a silica crucible. The melt is dissolved in a hot saturated solution containing 2 to 4 g. am-

[1] H. B. Weiser and E. E. Porter, *J. Phys. Chem.*, **31**, 1383, 1704 (1927).
[2] A. R. Powell and W. R. Schoeller, *Analyst*, **50**, 485 (1925); **57**, 550 (1932).
[3] A. R. Powell and W. R. Schoeller, *Z. anorg. u. allgem. Chem.*, **151**, 221 (1926).
[4] W. R. Schoeller, *Analyst*, **57**, 750 (1932).
[5] W. R. Schoeller and C. Jahn, *ibid.*, **59**, 465 (1934).
[6] L. Bleyenheuft, *Ing. chim.*, **20**, 165 (1936); *Chem. Abstracts*, **31**, 3817 (1937).
[7] W. R. Schoeller, chapter on columbium and tantalum in W. W. Scott, *Standard Methods of Chemical Analysis*. 5th ed., Van Nostrand, New York, 1939.

monium oxalate. A few drops of dilute sulfuric acid may be added to assist in dissolving the oxides. Any small residue is filtered, washed with hot water, ignited, and treated as before. The second ammonium oxalate solution, filtered if necessary to remove silica, is combined with the original filtrate and washings.

The solution of the combined filtrates is heated to boiling and 10 ml. freshly prepared 2% tannin is added. If the solution remains clear, 0.5 *N* ammonia is added carefully until a permanent turbidity is obtained. From the color of the precipitate at this point it is possible to estimate roughly the ratio of the metals. If the precipitate is yellow, the oxide mixture is at least one-third tantalic oxide; if it is orange, columbium predominates. More tannin is now added, depending on the amount of tantalic oxide present. For less than 30 mg. Ta_2O_5, the 10 ml. of tannin solution added initially is sufficient. For larger amounts, additional tannin should be used; the amounts are shown below:

Tantalic oxide, mg.	Additional 2% tannin required, ml.
30 or less	None
30–60	5–10
60–120	15–20
120–180	25–30
180–250	35–40

The reagent is added slowly; if the precipitate tends to become orange in color, no further addition is made. A saturated solution containing 5 g. ammonium chloride is added; the solution is boiled for about 10 minutes, and allowed to settle. The precipitate is collected on ashless paper and washed with hot 2% ammonium chloride. The determination is continued from this point by procedure A if the precipitate is orange to red in color, or by procedure B if it is yellow:

Procedure A. The filtrate and washings are boiled, treated with 5–10 ml. tannin solution, and neutralized with 0.5 *N* ammonia until the precipitate flocculates. After standing overnight, the precipitate is filtered and washed as before, and ignited with the first tantalum precipitate. The weighed impure tantalic oxide is then fused with pyrosulfate as at the beginning of the analysis, and the determination is carried out as before. Procedure B is then used in place of procedure A.

Procedure B. The filtrate is returned to the original beaker and concentrated about 25%. The wash solution from the first tantalum precipitation, to which several milliliters of tannin have been added, is mixed with the boiling filtrate, and 0.5 *N* ammonia is added slowly

until the orange color disappears. Saturated ammonium oxalate solution, in 10–25 ml. portions, is added until the yellow precipitate coagulates. After standing overnight, the precipitate is filtered, washed with 2% ammonium chloride solution, and ignited with the first precipitate. The filtrate from the second precipitation should be tested for tantalum by adding more ammonia and ammonium oxalate. Any yellow precipitate should be filtered and combined with the other tantalum precipitates. An orange precipitate indicates complete recovery of the tantalum, and may be disregarded.

Final determination of tantalum is made by leaching the ignited oxide with dilute acid (which is neutralized with ammonia before the oxide is filtered out) and igniting the precipitate strongly. The tantalic oxide is corrected for silica, calcium oxide, and titanium dioxide by fusion with bisulfate, treatment of the melt with ammonium oxalate, and determination of the insoluble portion. Tantalic oxide, Ta_2O_5, contains 81.89% tantalum.

Columbium is determined by difference, or by precipitation with ammonia from the tantalum filtrates. The ignited oxide must be corrected for impurities. The solution obtained by treating the bisulfate melt with oxalate is tested for titanium with hydrogen peroxide, and is then treated with tartaric acid, ammonia, and ammonium sulfide. The precipitate contains calcium, iron, and silica. Columbic oxide, Cb_2O_5, contains 69.90% columbium.

Methods have been reported for the determination of tantalum and columbium in titanocolumbate ores,[8] and in other minerals in which appreciable quantities of iron and titanium are present.[9] In the latter case the Schoeller method is modified to the extent that columbium and tantalum are separated, as soluble complexes, with pyrogallic acid from iron and titanium.

II. Determination of Tungsten[10–14]

When a neutral or alkaline tungstate solution containing tannin is

[8] V. S. Bykova, *Trudy Kol'skoi Bazy Akad. Nauk S.S.S.R.*, **1940**, No. 5, 77; *Khim. Referat. Zhur.*, **4**, No. 2, 61 (1941); *Chem. Abstracts*, **37**, 3008 (1943).
[9] I. P. Alimarin and B. I. Frid, *Trudy Vsesoyuz. Konferentsii Anal. Khim.*, **2**, 333 (1943); *Chem. Abstracts*, **39**, 3751 (1945).
[10] W. R. Schoeller and C. Jahn, *Analyst*, **52**, 506 (1927).
[11] L. Moser and W. Blaustein, *Monatsh.*, **52**, 351 (1929).
[12] W. R. Schoeller and E. F. Waterhouse, *Analyst*, **61**, 449 (1936).
[13] D. A. Lambie, *ibid.*, **64**, 481 (1939).
[14] H. E. Peterson and W. L. Anderson, U. S. Bur. Mines, Repts. *Investigations*, **3709**, 15 pp. (1943).

acidified with hydrochloric (or other) acid, precipitation of the major portion of the tungsten occurs. Some remains colloidally dispersed, however, either as the tannin complex or as tungstic acid. This colloid may be flocculated by adding a tannin precipitant such as an alkaloid. Substances commonly used in this connection are cinchonine ($C_{19}H_{22}N_2O$) and antipyrine (1,5-dimethyl-2-phenyl-3-pyrazolone, $C_{11}H_{12}N_2O$); others suggested include rhodamine B,[15, 16] β-naphthoquinoline,[17] and nemadine.[18] Of these, cinchonine is the best; antipyrine, however, may serve as a satisfactory substitute. Use of an insufficient quantity of alkaloid may prove to be a serious source of error in certain methods.

Using the tannin–cinchonine method, tungsten may be separated from aluminum, chromium(III), iron(III), phosphate, and many other ions.[11, 19] Double precipitations, however, are frequently required to obtain a final precipitate of tungstic oxide which is relatively free from interfering elements. The determination of tungsten in minerals, alloys, and salts of various sorts is often required. Preliminary steps in the analysis of tungsten-containing minerals may include an acid attack, or an alkali fusion, followed by one or more precipitations of the tungsten by the cinchonine method. Tungsten alloys may also be disintegrated with acid and the precipitated tungstic acid may be rendered completely insoluble by the addition of cinchonine. Details of a typical procedure are to be found on page 201.

The general method for precipitating tungsten from a solution of a soluble tungstate is as follows: The tungstate solution is made just acid to phenolphthalein and the volume is adjusted to about 150 ml. About 20 ml. 2.5% tannin solution is added, and the mixture is made acid to litmus with hydrochloric acid. The solution is boiled for 5 minutes, then 5 ml. cinchonine hydrochloride solution (125 g. cinchonine dissolved in 500 ml. hydrochloric acid, sp. gr. 1.19, and diluted with 500 ml. water) is added and the boiling is continued for 5 minutes longer. After standing for several hours or overnight, the precipitate is filtered and washed with 5% ammonium chloride solution containing a little tannin. The precipitate is ignited at 750°C. to tungstic oxide,

[15] J. T. Oats, *Eng. Mining J.*, **144**, 72 (1943).
[16] F. W. Box, *Analyst*, **69**, 272 (1944).
[17] B. A. Platunov and N. M. Kirillova, *Uchenye Zapiski Leningrad. Gosudarst. Univ., Ser. Khim. Nauk*, **1940**, No. 5, 260; *Khim. Referat. Zhur.*, **4**, 73 (1941); *Chem. Abstracts*, **37**, 4983 (1943).
[18] K. H. Gleason, *Eng. Mining J.*, **145**, 79 (1944).
[19] D. A. Lambie, *Analyst*, **68**, 74 (1943).

WO_3, which contains 79.30% tungsten. Ignition temperatures higher than 850° must be avoided, since the oxide is appreciably volatile under these conditions.

Cinchonine alone will complete the precipitation of tungstic acid. The tungstate solution, free from interfering elements and as concentrated as possible, is acidified with hydrochloric and nitric acids and boiled. The solution is diluted with about 350 ml. of water, and ashless filter paper pulp and 10 ml. cinchonine solution are added. The solution is stirred and digested at 60–70° for 30 minutes. The precipitate and paper pulp are collected on an 11-cm. ashless paper, and washed well with a solution prepared by diluting 10 ml. cinchonine solution to one liter with distilled water. The precipitate is ignited carefully as before, using a platinum dish if a correction for silica, etc., is to be made subsequently.

III. Determination of Uranium[20]

To the neutral or slightly acid solution of the uranyl salt is added 2 ml. 2% tannin for each 12 mg. uranium present. The solution is heated to boiling, and a 10% ammoniacal ammonium acetate solution is added until a chocolate-brown precipitate forms. After settling, the precipitate is filtered, washed with hot 1% ammonium acetate solution containing some ammonia, dried, and ignited to the tritaoctoxide, U_3O_8, which contains 84.8% uranium.

A study has been made of the separation of uranium from calcium and phosphorus by the tannin method.[21]

IV. Miscellaneous Determinations

Aluminum. Tannin precipitates aluminum quantitatively from ammonium acetate solution, and separates that element from beryllium.[22, 23] The proper *p*H for the separation is 4.6, at which value the precipitation of aluminum is quantitative. Beryllium precipitates at *p*H 4.9. Since ignition of the precipitate is required, as well as rather

[20] P. N. Das-Gupta, *J. Indian Chem. Soc.*, **6**, 763 (1929).
[21] L. E. Kaufman, *Zavodskaya Lab.*, **9**, 106 (1940).
[22] L. Moser and M. Niessner, *Monatsh.*, **48**, 113 (1927).
[23] M. L. Nichols and J. M. Schempf, *Ind. Eng. Chem., Anal. Ed.*, **11**, 278 (1939). See also, G. W. Sears and H. Gung, *ibid.*, **16**, 598 (1944).
[24] L. Moser and J. Singer, *Monatsh.*, **48**, 673 (1927).
[25] L. Moser and F. List, *ibid.*, **51**, 181 (1929).
[26] W. R. Schoeller and H. W. Webb, *Analyst*, **61**, 235 (1936).

careful adjustment of the *p*H, the method seems inferior to the 8-hydroxyquinoline method (see page 163).

Beryllium. Tannin precipitates beryllium from solutions having a *p*H of 5 or greater. Tannin has been used, not for the precipitation of beryllium, but to precipitate chromium, iron, thorium, titanium, tungsten, vanadium, and zirconium in the presence of beryllium.[24–26]

Copper. Precipitation of copper occurs from a hot ammonium acetate solution. The precipitate, which contains reduced copper, is ignited for final weighing.[27]

Gallium. The precipitation of gallium occurs in ammonium acetate solution, and permits the separation of gallium from beryllium, cadmium, cobalt, manganese, nickel, thallium, and zinc.[28] Presumably the alkaline earths and alkali metals do not precipitate under the conditions used. Gallium may be separated from iron after reducing the iron with $Na_2S_2O_4$.[29]

Manganese. Precipitation by tannin occurs from an ammoniacal solution of manganese(II) salts, but is not quantitative.[30]

Rare Earths. A method has been given for the separation of the rare earths from columbium and tantalum, using tannin.[31]

Titanium. The precipitation of titanium by tannin occurs in acetate solution: final weighing of the precipitate is as titanium dioxide. Methods describing the separation of titanium from columbium and tantalum,[32–34] and from zirconium and other elements[35–37] have been given.

Vanadium. Tannin precipitates alkali vanadates from acetate solution; the precipitate is ignited to vanadium pentoxide. By this reaction vanadium may be separated from beryllium,[38] and probably also from cadmium, nickel, and zinc.

Zirconium. A method has been given for the separation of zir-

[27] M. B. Darbinian and A. G. Kankanian, *Z. anal. Chem.*, **99**, 29 (1934).
[28] L. Moser and A. Brukl, *Monatsh.*, **50**, 181 (1928); **51**, 325 (1929).
[29] N. I. Vlodavets, *Trudy Inst. Geol. Nauk Akad. Nauk Soyuza S. S. R. Mineral. Geokhim, Ser.*, **1940**, No. 17 [No. 4], 1–18; *Chem. Abstracts*, **38**, 1445 (1944).
[30] W. R. Schoeller and H. W. Webb, *Analyst*, **59**, 667 (1934).
[31] W. R. Schoeller and E. F. Waterhouse, *ibid.*, **60**, 284 (1935).
[32] W. R. Schoeller and E. C. Deering, *ibid.*, **52**, 625 (1927).
[33] W. R. Schoeller and A. R. Powell, *ibid.*, **53**, 258 (1928).
[34] W. R. Schoeller and C. Jahn, *ibid.*, **54**, 320 (1929); **57**, 72 (1932).
[35] W. R. Schoeller and A. R. Powell, *ibid.*, **55**, 605 (1930).
[36] L. Moser, K. Neumayer, and K. Winter, *Monatsh.*, **55**, 85 (1930).
[37] W. R. Schoeller and H. W. Webb, *Analyst*, **58**, 143 (1933).
[38] L. Moser and O. Brandl, *Monatsh.*, **51**, 169 (1929).

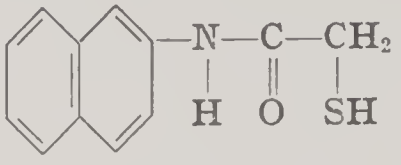
conium (and hafnium) from columbium and tantalum.[39] Zirconium is quantitatively precipitated by tannin in 0.25 to 0.5 *N* hydrochloric acid solution containing ammonium chloride. This reaction permits the separation of zirconium from thorium, uranium, and vanadium, but not from tin or titanium.[40]

[39] W. R. Schoeller and E. F. Waterhouse, *Analyst*, **53**, 515 (1928).
[40] W. R. Schoeller, *ibid.*, **69**, 259 (1944).

CHAPTER XIX

Thionalide

(Thioglycollic Acid, β-Aminonaphthalide)



Molecular weight: 217.1
Melting point: 111–112°C.
Solubility: soluble in ethyl and methyl alcohol, acetone, glacial acetic acid; insoluble in water, solutions of mineral acids
Reagent solution: 1 or 2% in ethyl alcohol, acetone, or glacial acetic acid; solution should be freshly prepared

Thionalide may be used for the precipitation and determination of elements of the hydrogen sulfide group; these elements include: antimony, arsenic, bismuth, copper, gold, mercury, palladium, platinum, silver, and tin. They are precipitated from acid solutions, while, from carbonate solution (containing tartrate), the reagent will precipitate cadmium, copper, gold, mercury(II), and thallium(I). Antimony, bismuth, gold, lead, thallium, and tin are precipitated from carbonate solution containing tartrate and cyanide; from strongly alkaline solution containing these ions, only thallium is precipitated.

As would be expected from their resemblance to the sulfides, the thionalates are very insoluble in water. Unlike the sulfides, however, the thionalates have definite compositions, and many of the salts may be weighed after drying at moderate temperatures. The silver salt is one of the few that require ignition. Since the thionalates are decomposed and oxidized rather easily by iodine, an iodimetric method for analyzing the precipitates may be used. The reaction for the oxidation of thionalide to dithionalide by iodine in glacial acetic acid, and in the presence of potassium iodide, is:

$$2\,C_{10}H_7NHCOCH_2SH + I_2 \rightarrow C_{10}H_7NHCOCH_2{-}S{-}S{-}CH_2CONHC_{10}H_7 + 2\,HI$$

Potassium iodate may be substituted for iodine.

Another volumetric method, the "filtration method," may also be used, but has found rather limited application to date (see page 161).

Because of the fact that thionalide is a reducing agent, solutions to which the reagent is added should be free from oxidizing ions. Hydroxylamine sulfate is generally used to reduce ferric and other oxidizing ions which might decompose the reagent.

Some advantages of the use of thionalide as a reagent to replace hydrogen sulfide are: (*1*) precipitations may be made in the presence of nitric acid, if it is not too strong; (*2*) coprecipitation phenomena are not encountered as in the case of many sulfide precipitations; (*3*) the reagent permits a separation of the elements of the hydrogen sulfide group from lead and cadmium—elements normally in that group; (*4*) the reagent is easy to use, the precipitates are stable, and the conversion factors are favorable; (*5*) excess precipitant is easily destroyed in the filtrate from a thionalide precipitation by oxidation with iodine.

In many cases, however, the use of thionalide offers no advantage over methods employing other reagents. Thus, the determination of copper and its separation from other elements may be less convenient when thionalide is used than when salicylaldoxime or quinaldic acid is used. The reasons for this are that the copper thionalate is difficult to filter, and that chlorides in large amounts exercise a disturbing effect. In other cases useful separations may be made, as in the separation of silver from lead and thallium, and the separation of thallium from antimony, arsenic, copper, silver, and other metals (see page 279). In the following sections details of some of the typical determinations using thionalide will be given.

I. Determination of Copper[1]

Copper may be separated from the alkaline earths and alkali metals, aluminum, cadmium, chromium(III), cobalt, iron(II), lead, manganese(II), nickel, and zinc (and perhaps others) by this procedure. As much as 460 mg. thallium, 300 mg. iron, or 100 mg. of each of the other elements listed may be present in solutions containing up to 100 mg. copper.

The solution containing copper should be no stronger than 0.5 *N* in nitric or sulfuric acid; the optimum concentration is 0.1 *N*. High values are obtained if very strong acid is used. Chlorides should be absent, or present at most in small amounts, or high results will fol-

[1] R. Berg and O. Roebling, *Angew. Chem.*, 48, 597 (1935).

low. If oxidizing agents are present as well as chlorides, the reduction with hydroxylamine sulfate should not be carried out until the solution has been fumed with sulfuric acid, because insoluble cuprous chloride may form, leading to low results.

The solution, containing no more than 100 mg. copper, is heated to about 80°C., and 10 ml. 1% thionalide in alcohol is added for each 10 mg. copper estimated to be present; the total volume may be from 200 to 250 ml. The solution is stirred to coagulate the precipitate and filtered while hot through a warm filtering crucible to insure rapid filtration. The precipitate is washed with hot water and dried at 105° to constant weight. The precipitate, $Cu(C_{12}H_{10}ONS)_2 \cdot H_2O$, contains 12.37% copper.

Volumetric Determination. The precipitate is collected on paper rather than on a filtering crucible. After washing, the precipitate and paper are returned to the precipitation beaker and treated with 50 ml. glacial acetic acid, 5 ml. dilute sulfuric acid, 0.1 g. potassium iodide, and 10 ml. 1 *N* ammonium thiocyanate. Excess 0.02 *N* iodine solution is added, the solution is diluted to about 150 ml., and the excess iodine is titrated with 0.02 *N* thiosulfate. One milliliter 0.02 *N* iodine is equivalent to 1.272 mg. copper.

II. Determination of Silver[1]

The thionalide procedure is of value in cases in which silver is to be separated from thallium and lead. Up to 50 mg. silver may be separated from a maximum of 460 mg. thallium, or 2 g. lead. The method for precipitating silver is the same as that for copper, given above. The complex is collected on filter paper, washed, ignited to metallic silver, dissolved in nitric acid, and converted to silver chloride, which is weighed. Silver chloride contains 75.26% silver.

The volumetric method is probably faster than the gravimetric method in this case. The determination is carried out in the manner described for copper, except that no thiocyanate is added. One milliliter 0.02 *N* iodine is equivalent to 2.158 mg. silver.

III. Determination of Mercury[1]

Mercury is precipitated from an acid solution in which the concentration of chloride ion should be no greater than 0.1 *N*, or preferably just equivalent to the mercury present. This avoids the danger of precipitating calomel if prior reduction of iron must be made. The so-

lution may contain up to 100 mg. mercury; separation from as much as 400 mg. of iron, and 100 mg. each of calcium, magnesium, etc. (as listed previously in the case of copper), also may be made.

The precipitation is carried out in the manner described for copper. A threefold excess of precipitant should be used. After washing and drying at 105°, the complex $Hg(C_{12}H_{10}ONS)_2$ is weighed; it contains 31.69% mercury. The precipitate may be analyzed volumetrically as in the other cases. One milliliter 0.02 *N* iodine is equivalent to 2.005 mg. mercury.

IV. Determination of Bismuth[1]

Bismuth may be precipitated from acid solution, or from an alkaline solution containing tartrate and cyanide. The latter reaction separates bismuth from aluminum, arsenic, cadmium, chromium, cobalt, copper, iron, mercury, nickel, palladium, platinum, silver, titanium, vanadium, and zinc. The precipitation of bismuth is complicated by the fact that, in an acid solution in the presence of chlorides or sulfates, basic salts may form that will produce low results. In the following descriptions, the first procedure is for cases in which nitrate is the only anion present; the second procedure is for cases in which chloride or sulfate may be present.

A. Precipitation in Acid Solution

(*1*) To the solution containing 20 to 100 mg. bismuth and not more than 300 mg. iron, 1 g. lead or cadmium, and 100 mg. of each of the elements listed in the above paragraph, ammonium or sodium hydroxide is added until a turbidity in the solution persists. Then 3–5 ml. 2 *N* nitric acid is added for each 100 ml. of solution, and the bismuth is precipitated, as described for copper, with a fourfold excess of reagent. The solution is allowed to stand on a steam bath for 20–30 minutes and is stirred frequently to coagulate the precipitate. When the supernatant liquid is clear, the precipitate is collected on a filtering crucible of fine porosity, washed, and dried at 100°C. The complex, $Bi(C_{12}H_{10}ONS)_3$, contains 23.87% bismuth.

(*2*) The acid bismuth solution, containing chloride or sulfate, is neutralized with ammonium or sodium hydroxide until a permanent turbidity is obtained. The foreign elements listed in (*1*) above may be present. To the solution is then added 10 ml. 2 *N* nitric (or sulfuric) acid per 100 ml. and the bismuth is precipitated with a fourfold excess

of reagent. Immediately after precipitation, the solution is partially neutralized by adding 5 ml. 2 *N* sodium hydroxide for each 100 ml. total volume. The determination is concluded as in (*1*). A maximum of about 2 g. of sodium chloride, or its equivalent, can be present with 20-mg. bismuth samples without making the results low.

The volumetric method, if used, must be carried out in a solution saturated with ammonium chloride. One milliliter 0.02 *N* iodine is equivalent to 1.393 mg. bismuth. This method is of particular interest for the determination of bismuth in fusible alloys, where a sharp separation from cadmium and lead is required.

B. Precipitation in Tartrate–Cyanide Solution[2]

Amounts of bismuth up to 50 mg. may be separated from the elements mentioned previously (page 276), present in amounts up to 1 g. each. Gold, lead, tin(IV), thallium, and antimony(III) interfere.

To the nitric acid solution of bismuth and other elements is added 10–20 ml. 20% sodium tartrate solution (20 ml. is sufficient for a 0.5 g. sample), followed by 2 *N* sodium carbonate until the phenolphthalein end point is reached. A quantity of potassium cyanide sufficient to complex the foreign elements is then added; this usually amounts to 40–50 ml. 20% solution. More sodium carbonate is added until the solution is about 1 *N*. The total volume should be between 100 and 300 ml. at this point. To the cold solution a fourfold excess of thionalide is added, with stirring. The solution is heated to boiling, and the stirring is continued until the precipitate becomes crystalline. The solution is cooled to room temperature and decanted through a fine sintered-glass crucible. The precipitate is washed by decantation with cold water until it is free from cyanide (the washings should give no reaction with silver nitrate) and is then transferred to the crucible. The precipitate is then washed with several small portions of 10% alcohol to remove excess thionalide. The filtrate should give no turbidity when diluted with 3 volumes of water, acidified with sulfuric acid, and treated with a few drops of 0.1 *N* iodine solution. The precipitate is dried to constant weight at 105° and weighed as $Bi(C_{12}H_{10}ONS)_3$, containing 24.36% bismuth. When the quantity of foreign elements exceeds 1 g., the bismuth complex should be dissolved in acetone after being filtered and washed. To the acetone solution 100 ml. 5% potassium cyanide containing 2 g. sodium tartrate is then

[2] R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **112**, 161 (1938).

added. The acetone is boiled off, and bismuth is precipitated from the solution as before.

V. Determination of Lead[2]

By following a procedure of the same general type as for bismuth (page 277), lead in amounts from 3 to 50 mg. may be separated from aluminum, arsenic, cadmium, chromium(III), cobalt, copper, iron(II), nickel, silver, titanium(IV), and zinc. Less than 4% chloride, or 1% sulfate, must be present in the solution, if at all. The details of the procedure differ from those given for bismuth only in that the precipitate of $Pb(C_{12}H_{10}ONS)_2$ is washed with 50% acetone rather than with alcohol. The precipitate, dried at 105°C. contains 32.40% lead.

VI. Determination of Antimony[2]

Antimony(III) may be separated from cerium(III), chromium(III), cobalt, iron(II), and titanium(IV), by precipitating $Sb(C_{12}H_{10}ONS)_3$ under conditions which are the same as those used for bismuth and lead. The precipitate is washed with 10% alcohol and dried at 100°; it contains 15.81% antimony. Arsenic, bismuth, cadmium, gold, lead, mercury, thorium, and tin interfere, as do the alkaline earths.

VII. Determination of Thallium[3]

Thallium is quantitatively precipitated as $Tl(C_{12}H_{10}ONS)$ from an alkaline solution containing cyanide, or tartrate, in relatively large amounts, and may thus be separated from a number of elements which are not precipitated under similar conditions. These elements include aluminum, antimony, arsenic, bismuth, cadmium, cobalt, copper, gold iron, lead, mercury, molybdenum, nickel, palladium, platinum, silver, tellurium, tin, tungsten, uranium, vanadium, and zinc. Separation is also made from the alkali metals, and from the alkaline earths in carbonate-free solution.

A. Determination of Thallium in Pure Solutions

The acidic solution, containing from 25 to 100 mg. thallium, is neutralized with 2 *N* sodium hydroxide; then 2 g. sodium acetate and 3–5 g. potassium cyanide are added. Sufficient 2 *N* sodium hydroxide is then added to make the solution approximately 1 *N*, and the volume is adjusted to about 100 ml. A four- to fivefold excess of thionalide in

[3] R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **109**, 305 (1937); *Mikrochim. Acta*, **1**, 64 (1937).

acetone is added to the cold solution. The solution is then heated to boiling, and stirred to coagulate the precipitate. When the precipitate has become crystalline, the solution is cooled to room temperature and the precipitate is collected on a filtering crucible of fine porosity and is washed free from cyanide with cold water, then free from thionalide with acetone. The precipitate, dried at 100°, contains 48.60% thallium.

If the precipitate is to be titrated, it is collected on filter paper, washed with water and acetone, and returned along with the paper to the original beaker. A mixture of 3 parts glacial acetic acid and 1 part 2 *N* sulfuric acid is added; 40 ml. of the mixture is sufficient to dissolve about 40 mg. of precipitate. Standard iodine solution, about 0.02 *N*, is added in excess; the mixture is stirred well, and the excess iodine is titrated with thiosulfate. One milliliter 0.02 *N* iodine is equivalent to 4.09 mg. thallium.

B. Determination of Thallium in the Presence of Other Elements

Separation may be made from the elements listed at the beginning of the section, page 278. Oxidizing ions must first be reduced with hydroxylamine to prevent oxidation of the reagent. If the alkaline earth elements are present, carbonate-free conditions must be maintained. Uranium, if present, will probably precipitate with the thallium as sodium uranate; this is removed subsequently from the thallium precipitate by washing with 10% ammonium carbonate. Mercury, bismuth, and lead are coprecipitated to some extent under the conditions used. However, since the thionalates of these metals are soluble in acetone, interference can be avoided by adding a tenfold excess of precipitant and sufficient acetone to make the concentration 30%. If mercury is present, an additional 4 g. potassium cyanide should be added.

To the thallium solution is added 5 g. sodium tartrate per 100 ml. and the solution is neutralized with 2 *N* sodium hydroxide to the phenolphthalein end point. After 5 g. potassium cyanide per 100 ml. is added, the alkalinity is adjusted to about 1 *N*, and thallium is precipitated in the cold with a four- to fivefold excess of 5% thionalide in acetone. For 100 mg. thallium, 400 to 500 mg. thionalide should be added. The solution is heated to boiling, with stirring to coagulate the precipitate. When the precipitate has become crystalline, the solution

is cooled to room temperature and filtered through a filtering crucible of fine porosity. The precipitate is washed with cold water until free from cyanide, and then with acetone until free from thionalide. The precipitate, dried at 100°C. contains 48.60% thallium.

The volumetric method may be employed; see page 275.

VIII. Determination of Platinum Metals

Thionalide combines with ions of the platinum metals to give insoluble compounds, and use has been made of this property in the determination of rhodium[4] and ruthenium.[5]

A. Determination of Rhodium

The chloride-free rhodium solution, 30 to 50 ml. in volume and containing 0.25 to 10 mg. rhodium, is treated with an excess of 1–2% thionalide in acetic acid. The solution is heated to boiling; the orange-yellow precipitate that forms is filtered hot and is then washed with a few milliliters of acetic acid. Thionalide is determined in the filtrate by the addition of excess standard iodine solution, followed by thiosulfate titration. The thionalide solution is standardized in the same manner. The maximum error, on samples of the size indicated, is about 1%.

B. Determination of Ruthenium

The precipitation of ruthenium is quantitative in solutions 0.2 to 0.5 *N* in hydrochloric acid. Precipitation with thionalide generally follows the separation of ruthenium from other metals by distillation from a sulfuric acid solution containing sodium bromate. The volatile ruthenium tetroxide is absorbed in hydrogen peroxide solution.

The sample, containing up to 15 mg. of ruthenium, is made up to about 200 ml.; 10 ml. of sulfuric acid is added, and the mixture is placed in the distillation apparatus (similar to Scientific Glass Apparatus Co. Still No. J1306). Two receiving flasks contain 35 ml. and 15 ml., respectively, of 3% hydrogen peroxide, free from acetanilide. To the distillation flask is added several grams of sodium bromate, and the ruthenium tetroxide is removed by distillation for 2 hours. The hydrogen peroxide absorbents are combined, diluted to about 150 ml., and, after addition of 0.6 ml. hydrochloric acid, are heated to

[4] H. Kienitz and L. Rombock, *Z. anal. Chem.*, **117**, 241 (1939).
[5] W. J. Rogers, F. E. Beamish, and D. S. Russell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 561 (1940).

boiling to decompose the peroxide. An excess of thionalide in alcohol is then added (8–10 mg. thionalide per mg. ruthenium) and the solution is boiled until the precipitate coagulates. The complex is filtered on ashless paper, washed with hot water, and dried along with the paper. When completely dry, the paper and contents are charred, and are then finally ignited strongly for 2 minutes. The residue is reduced in hydrogen, cooled, and weighed as metallic ruthenium. With semimicro quantities the results tend to be low—the maximum error amounting to about 10%.

APPENDIX

TABLE XXX

Drying Temperatures and Conversion Factors

Precipitate	Drying temperature, °C.	Conversion factor (to metal or anion)
Anthranilic acid		
$Cd(C_7H_6NO_2)_2$	105–110	0.2922
$Co(C_7H_6NO_2)_2$	105–110	0.1780
$Cu(C_7H_6NO_2)_2$	105–110	0.1838
$Zn(C_7H_6NO_2)_2$	105–110	0.1936
Benzoin oxime		
$Cu(C_{14}H_{11}NO_2)$	105–110	0.2201
Dimethylglyoxime		
$Ni(C_4H_7N_2O_2)_2$	110–120	0.2032
$Pd(C_4H_7N_2O_2)_2$	110	0.3167
8-Hydroxyquinoline		
$Al(C_9H_6NO)_3$	140	0.0587
$Cd(C_9H_6NO)_2$	130	0.2806
$Cu(C_9H_6NO)_2$	105–110	0.1808
$Mg(C_9H_6NO)_2$	160	0.0778
$Zn(C_9H_6NO)_2$	160	0.1850
Furfuraldoxime		
$Pd(C_6H_5NO_2)_2Cl_2$	110	0.2669
Dipicrylamine		
$KC_{12}H_4N_7O_{12}$	110	0.0819
8-Quinolinecarboxylic acid		
$Cu(C_{10}H_6NO_2)_2$	110–120	0.1558
Nitron		
$C_{20}H_{16}N_4 \cdot HNO_3$	110	0.1653
$C_{20}H_{16}N_4 \cdot HReO_4$	110	0.4442
Triphenyltin chloride		
$C_{18}H_{15}SnF$	110	0.05153
Quinaldic acid		
$Cd(C_{10}H_6NO_2)_2$	125	0.2462
$Cu(C_{10}H_6NO_2)_2 \cdot H_2O$	110–115	0.1494
$Zn(C_{10}H_6NO_2)_2 \cdot H_2O$	125	0.1529
Salicylaldoxime		
$Cu(C_7H_6NO_2)_2$	100–105	0.1894
$Pb(C_7H_5NO_2)$	105	0.6040
$Pd(C_7H_6NO_2)_2$	110	0.2817
$Zn(C_7H_6NO_2)_2$	105	0.1938
$Zn(C_7H_5NO_2)$	105	0.3263
Thionalide		
$Sb(C_{12}H_{10}ONS)_3$	100	0.1581
$Bi(C_{12}H_{10}ONS)_3$	100	0.2387
$Cu(C_{12}H_{10}ONS)_2 \cdot H_2O$	105	0.1237
$Pb(C_{12}H_{10}ONS)_2$	105	0.3240
$Hg(C_{12}H_{10}ONS)_2$	105	0.3169
$Tl(C_{12}H_{10}ONS)$	100	0.4860

TABLE XXXI

Elements Determined Gravimetrically and Volumetrically by Organic Reagents

Element	Reagent
Aluminum	Cupferron
	8-Hydroxyquinoline
	Tannin
Antimony	8-Hydroxyquinoline
	Phenylthiohydantoic acid
	Thionalide
Arsenic	8-Hydroxyquinoline
	Thionalide
Barium	8-Hydroxyquinoline
	Picrolonic acid
	Tannin
Beryllium	8-Hydroxyquinoline
	Tannin
Bismuth	Cupferron
	8-Hydroxyquinoline
	Mercaptobenzthiazole
	Phenylthiohydantoic acid
	Thionalide
Cadmium	Anthranilic acid
	8-Hydroxyquinoline
	Mercaptobenzthiazole
	Quinaldic acid
	Tetraphenylarsonium chloride
Calcium	8-Hydroxyquinoline
	Picrolonic acid
Cerium	8-Hydroxyquinoline
	Tannin
Chromium	8-Hydroxyquinoline
Cobalt	Anthranilic acid
	8-Hydroxyquinoline
	α-Nitroso-β-naphthol
	Phenylthiohydantoic acid
Columbium	Cupferron
	8-Hydroxyquinoline
	Phenylarsonic acid
	Tannin
Copper	Anthranilic acid
	Benzildioxime
	Benzoin oxime
	Cupferron
	8-Hydroxyquinoline
	8-Hydroxyquinaldine
	Mercaptobenzthiazole
Copper (*continued*)	Quinaldic acid
	Quinoline-8-carboxylic acid
	Salicylaldoxime
	Tannin
	Thionalide
Fluorine	Triphenyltin chloride
Gallium	Cupferron
	8-Hydroxyquinoline
	Tannin
Gold	Dimethylglyoxime
	Thionalide
Indium	8-Hydroxyquinoline
Iron	Butylphenylarsonic acid
	Cupferron
	8-Hydroxyquinoline
	α-Nitroso-β-naphthol
	Tannin
Lead	8-Hydroxyquinoline
	Mercaptobenzthiazole
	Picrolonic acid
	Salicylaldoxime
Magnesium	8-Hydroxyquinoline
	Picrolonic acid
Manganese	Anthranilic acid
	8-Hydroxyquinoline
Mercury	Anthranilic acid
	Cupferron
	8-Hydroxyquinoline
	Tetraphenylarsonium chloride
	Thionalide
Molybdenum	Benzoinoxime
	8-Hydroxyquinoline
	Tannin
Nickel	Anthranilic acid
	Dimethylglyoxime
	Furildioxime
	Salicylaldoxime
Nitrogen (nitrate)	Nitron
Palladium	Anthranilic acid
	Dimethylglyoxime
	Furildioxime
	8-Hydroxyquinoline
	Salicylaldoxime
	Thionalide

TABLE XXXI (*continued*)

Element	Reagent
Phosphorus (phosphate)	Benzidine 8-Hydroxyquinoline
Platinum	Dimethylglyoxime Furildioxime
Potassium	Dipicrylamine
Rare Earths	8-Hydroxyquinoline
Rhenium	Nitron
Rhodium	Thionalide
Ruthenium	Thionalide
Silicon	8-Hydroxyquinoline
Silver	Thionalide
Strontium	8-Hydroxyquinoline Picrolonic acid Tannin
Sulfur (sulfate)	Benzidine
Tantalum	Cupferron Phenylarsonic acid Tannin
Thallium	Mercaptobenzthiazole Thionalide
Thorium	8-Hydroxyquinoline Picrolonic acid
Tin	Cupferron Hydroxyphenylarsonic acid
Tin (*continued*)	Phenylarsonic acid Tetraphenylarsonium chloride
Titanium	Cupferron 8-Hydroxyquinoline Tannin
Tungsten	Antipyrine Benzidine 8-Hydroxyquinoline Nitron Tannin
Uranium	Cupferron 8-Hydroxyquinoline Quinaldic acid Tannin
Vanadium	Cupferron 8-Hydroxyquinoline Tannin
Zinc	Anthranilic acid Cupferron 8-Hydroxyquinoline Quinaldic acid Salicylaldoxime Tetraphenylarsonium chloride
Zirconium	Arsonic acids Cupferron 8-Hydroxyquinoline Tannin

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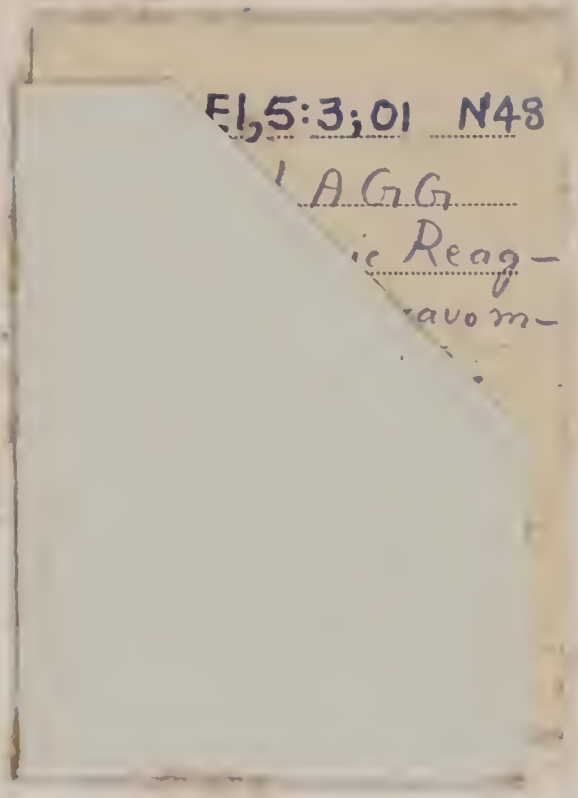
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